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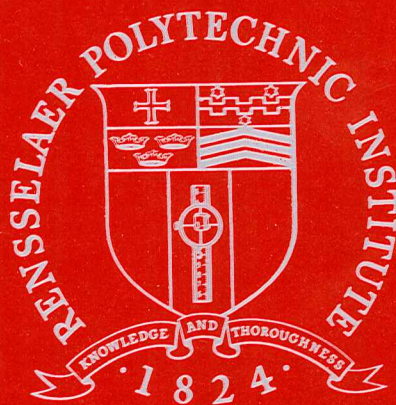
REDUCTION OF CHROMATOGRAPHIC DATA AND
EVALUATION OF A GC MODEL

Gordon L. Benoit

N71-35514

National Aeronautics and Space
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Rensselaer Polytechnic Institute
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Analysis and Design of a Capsule Landing System
and Surface Vehicle Control System for
Mars Exploration

June, 1971

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Troy, New York

ABSTRACT

The initial unmanned missions to Mars will require a gas chromatograph, mass spectrometer system to make determinations concerning the existence of certain chemical and biochemical species on the planet. It is the overall objective of this project to generate fundamental engineering design techniques and concepts for use in optimizing the design of the chromatograph. This particular task has as its objective the completion of an experimental system for generating gas chromatographic data and the development of numerical procedures for comparing the data with proposed GC mathematical models.

A previously used commercial chromatographic system was rejuvenated and modified. The system now features micro thermal conductivity detectors, an automatic injection valve, and inlet and output signal detection capability. A data reduction program has been written to compare the mathematical impulse response to the actual system data. The program convolves the normalized impulse response with the input function to give the convolved response which is compared to the actual data which has been normalized. Simpson's method is used for integration and a modified regula-falsi 1st order iteration scheme is employed to determine a system parameter by curve fitting. The program is capable of comparing any model to actual system data.

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I. INTRODUCTION

One important phase of the unmanned missions to Mars is the search for organic matter and living organisms on the Martian surface. The present concept for attaining this objective consists of subjecting samples of the atmosphere and surface matter to certain biological and chemical reactions and thereafter analyzing the products produced (1,2,3). The most likely system for a general chemical analysis appears to be a combination gas chromatograph-mass spectrometer GC-MS (4,5,8). This unit would be a major component in the biological and chemical laboratory of an unmanned, computer-controlled, roving lander for Mars. It is the overall objective of the Chromatographic Systems Analysis program to generate fundamental engineering design techniques and system concepts for use in optimizing the design of such a chromatograph separation system. Such a system should provide maximum resolution with minimum retention times and minimum carrier gas usage, and should be capable of separating components evolved from many different types of experiments.

The mechanisms involved in chromatographic separations are shown schematically in Figure 1. A gas chromatograph is generally a long piece of tubing filled with some packing. This packing may take the form of a porous granular or a liquid phase coated on some solid substrate. A non-adsorbing carrier gas is continually flowing through the column. The packing may be kept at a constant temperature, or the temperature may be continuously varied, which is called temperature programming. At time equal to zero the gaseous mixture to be separated is introduced into the column entrance. This mixture will be axially transported down the column by turbulent and molecular diffusion as is

CHROMATOGRAPHIC COLUMN CONCEPTS

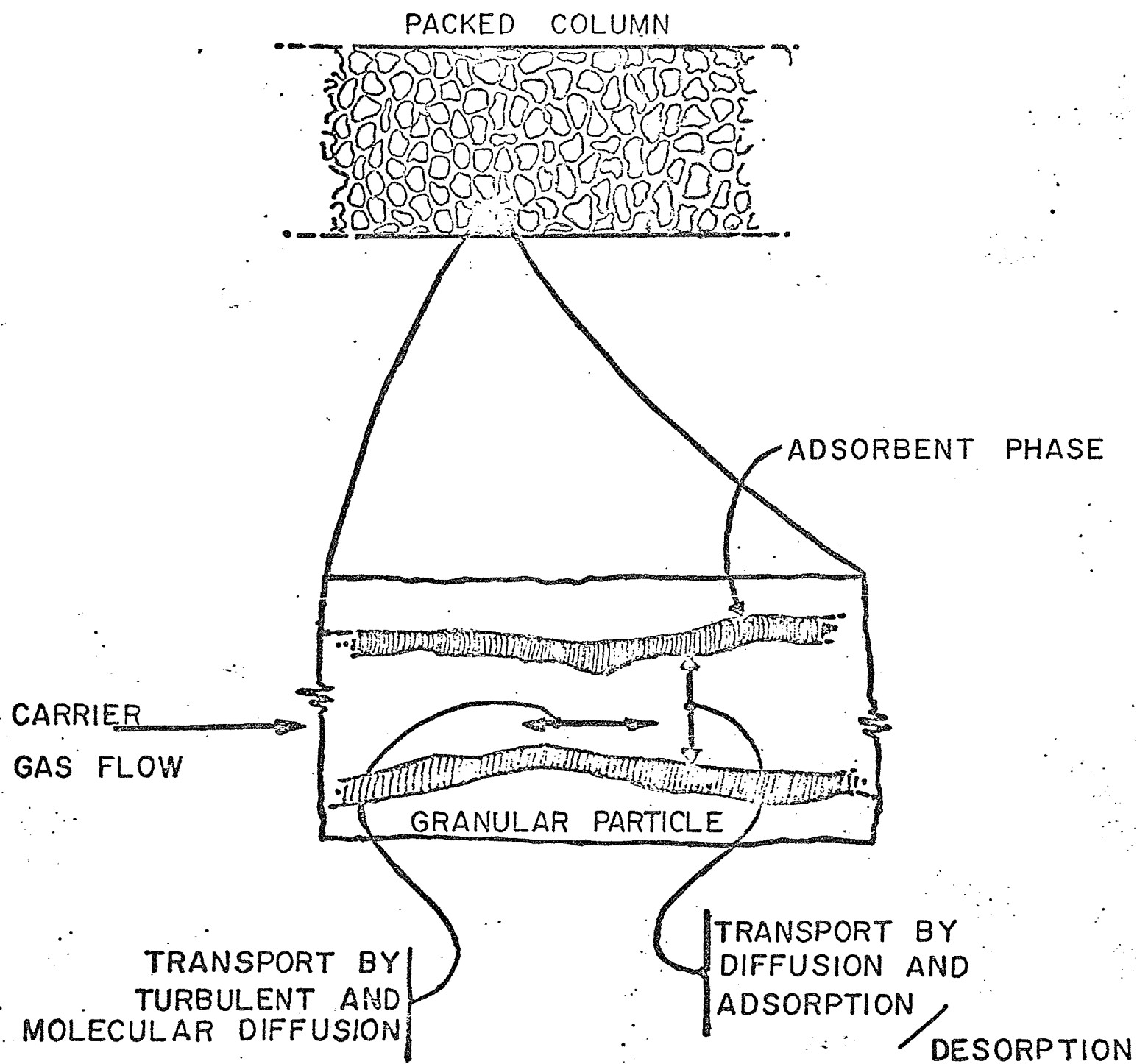


FIGURE 1

shown in the diagram. A properly selected column packing will selectively adsorb and desorb components in the mixture at different rates. In this manner some components are held in the column, on the average, a much longer time than other components and the mixture is separated. Total separation of a mixture into distinct molecular species is only achieved if the column or columns used are selective enough to adsorb and desorb each different compound in the mixture at a significantly different rates. Since this is rarely achieved in complicated mixtures with one column, parallel and series arrangements of columns are often used.

Because of the variety of mixtures to be separated and the complexity of the fractionating process, a system analysis based upon mathematical simulation of the chromatograph is being undertaken. This technique uses mathematical models, which incorporate fundamental parameters, to explore various concepts and to direct experimental research. Certain of these parameters are predictable a priori from the fluid mechanics characteristics, while others are peculiar to the specific system considered and are derived from experimental data. By using theoretical concepts as well as experimental data, it is hoped that the optimization of a particular system can be accomplished with more confidence than if experimental results are used alone.

Prior work has produced several mathematical models for evaluation (1,6,7). These models were solved from the basic second order, partial differential equation characterizing the chromatographic process. These equations were solved analytically by classical techniques and thus received certain simplifying assumptions. In particular, all of the models were solved assuming an impulse function input to the column.

The major objective of this project is to develop a method of evaluating these models. The construction of an experimental test facility was the first goal. Work was started in this area during the previous year, and was finished during the past fall (25). Important design requirements of the system included the following: rapid detector response, small system dead volume, record of both the input and output curves from the column, rapid recorder response, and predictable system parameters to facilitate comparison of the data to the models. The system is a modified Perkin Elmer Model 154 Fractometer employing Carle microdetectors, sample injection by syringe or a gas sampling valve, and signal recording by a Honeywell Oscillograph. It is described briefly in a following section.

After the test system was completed, the remainder of the year was devoted to developing a computer program capable of comparing the mathematical models with the actual data from the test facility. Given input data to the column, the system output data, system parameters, and a mathematical model for the impulse response of the column, it is necessary to convert the system parameters to model parameters, adjust the impulse response to take into account a finite input, and finally to digitally compare the model to the actual data. The philosophy of simulating the system performance, using the given input data, is followed. Convolution of the impulse response with the actual system input function is used to account for the way the gas mixture enters the column. System parameters are estimated from existing correlations, or are obtained from the actual data by a curve-fitting technique.

In this study, one of the models being considered is evaluated using the data reduction program. This model, the equilibrium adsorption model (6), assumes that any point in the column the gas phase of any component is in equilibrium with the liquid phase of the packing. This is equivalent to an infinitely long column. This assumption leads to a simple exponential solution to the governing equations:

$$Y/A = (1/2) \sqrt{\frac{\beta P_e}{\pi \theta^3}} \exp \left[-\frac{P_e}{4\beta} (\theta - \beta)^2 / \theta \right]$$

where

$$\beta = 1 + (1/mR_0)$$

and

P_e = the Peclet number which is a dimensionless measure of sample diffusion in the carrier gas.

mR_0 = a thermodynamic parameter, peculiar to the specific chemical species and adsorbent used.

θ = dimensionless time = vt/L

v = carrier gas velocity

t = time

L = column length

The dimensionless Peclet number is predictable since it depends only upon the system configuration and fluid mechanics. The thermodynamic parameter mR_0 is specific to the system used and is determined from the system data using a curve fitting technique.

Because of its simplicity, the above model is probably not an accurate representation of all systems, but it shows the desired characteristics and is useful in validating the data reduction and simulation procedures.

II. TEST FACILITY

A gas chromatograph (GC) offers a method of separating a gaseous mixture into subgroups having similar chemical properties. In the presence of an inert carrier gas, the various subgroups have different dynamic adsorption characteristics for a given column packing material. These different characteristics are responsible for the ability of the GC to separate the mixture, and the resulting changes in gas composition can be related to concentrations of each component in the initial mixture.

Any gas chromatograph system consists of six basic elements:

1. A regulated carrier gas supply.
2. A method of sample injection.
3. A means of detecting composition changes at the column outlet.
4. A chromatographic column.
5. A signal recording device.
6. A temperature-controlled oven chamber.

The gas chromatograph presently being used in the test facility is a modified Perkin Elmer Model 154 Vapor Fractometer. The system is not to simulate an actual gas chromatograph suitable for the Mars mission, but rather is to produce well-defined, reproducible data for evaluating mathematical models and to investigate various processing concepts. Hence a commercial system was acceptable providing modifications were made to give desirable characteristics:

1. Rapid detector response.
2. Detection of both inlet and outlet composition signals.
3. Rapid recorder response.
4. Minimum sample dead time, thermal transients and detector drift.

The major redesign objective of the test facility is to eliminate all unnecessary delays in the system so that the actual recorded output is as close to the actual composition variation as is physically possible. Because the mathematical models assume an impulse input, it is necessary to record both input and output composition variations. The actual input data are then used to mathematically adjust the model to account for the actual input behavior. This is done in the data reduction program described later, using the input function data from the test facility recording.

The system has been described in detail previously (25) so only the important features are presented here. The flow diagram modified system is shown in Figure 2. Helium is used in the system as the inert carrier gas. It was chosen because of its non-explosive nature, and its high thermal conductivity. The helium is regulated from 10 to 175 cc/min at 70°F by the system pressure regulator. The flowrate is recorded by a Brooks Rotometer located downstream from the regulator. The carrier gas then flows through the reference side of both detectors. These are thermal conductivity detectors which operate on the principle that the thermal conductivity of each component of a gas mixture is unique (13,14). If the thermal conductivity of the detector sample side differs from that of the reference side of the detector cell, a signal is generated in a Wheatstone bridge circuit connected to the detectors. This signal may be attenuated from 1 to 1000 times before being sent to a Honeywell Oscillograph for recording. Since two detectors are employed, two separate Wheatstone Bridge circuits are used, each being driven by the same 10 VDC source. The two signals are recorded simultaneously by the light beam oscillograph.

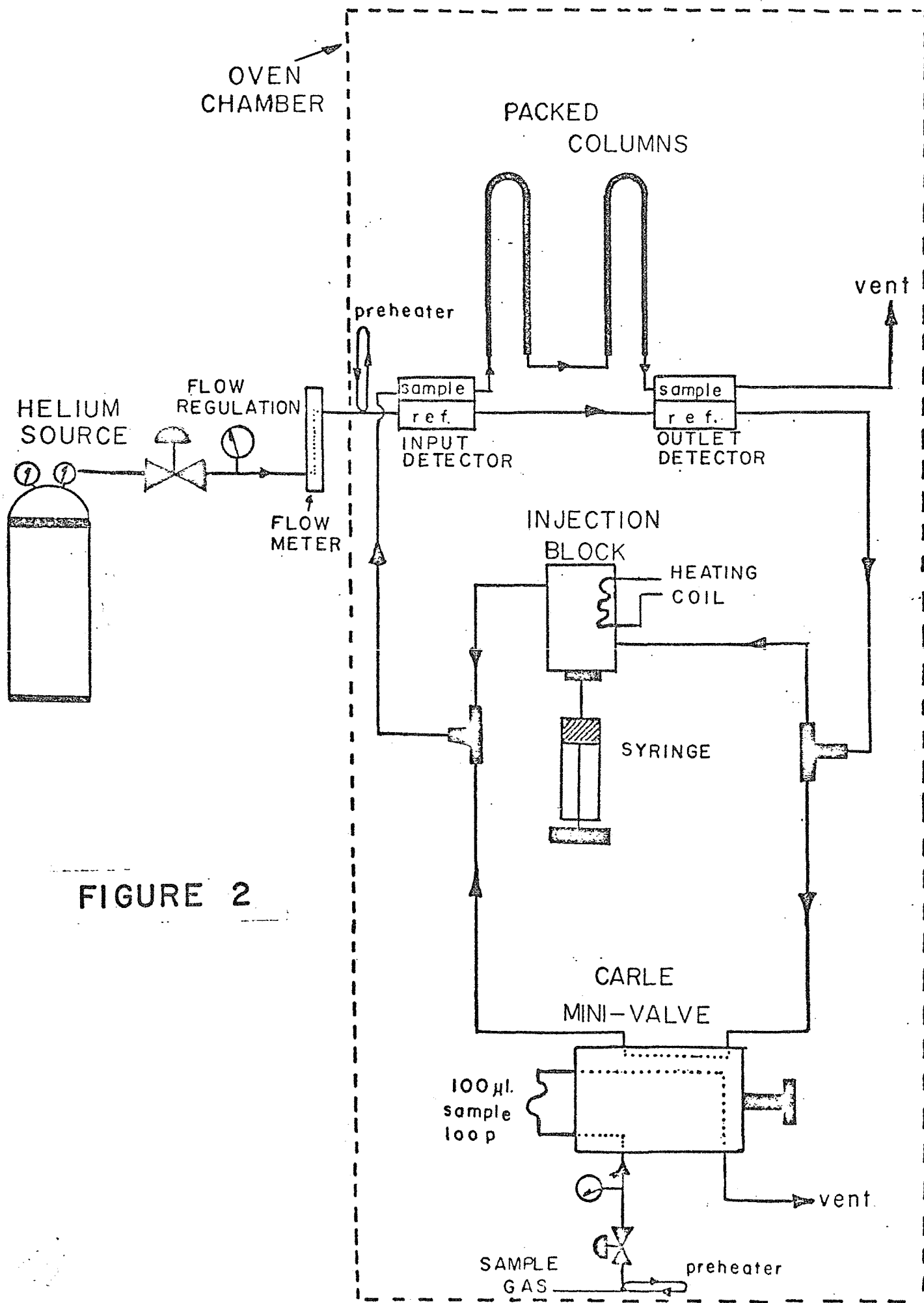


FIGURE 2

A gas sample is introduced into the carrier gas stream by one of three methods. For injection of a liquid mixture, a syringe is used to inject the mixture into the injection block, where the sample is vaporized by a small heater. A gas sample may also be directly injected into the block from a gas tight syringe. For gas samples from lecture bottles, a Carle Minivalve is used for injection. The schematic of this system is shown in Figure 3. The valve itself is similar to the actual injection system to be employed in the Mars mission. A gas sample of a specified volume is diverted into the carrier gas stream when the polarity of the valve is changed. The operation of the valve is shown in Figure 4. Experimental results indicate that the pulse sent to the column using this valve very closely approximates a rectangular pulse and is not as disperse as those obtained from syringe injection.

After injection, the sample passes through the inlet detector and then into the column. The column mounting bracket is designed to allow the use of two columns if necessary. This will allow either parallel or series operation of a complicated column system so other concepts can be studied. The separated sample then passes through the outlet detector where the actual gas chromatogram is recorded and is then vented.

The thermal control of the column and detector blocks is achieved through the use of an on-off controller which is connected through a variable load to the heating coil. The controller uses a signal from a thermistor located in the oven to adjust the heating load and thus control the oven temperature. The temperature in the oven is monitored by three thermocouples and a gas bulb thermometer all located in the oven chamber. Preheaters in both the carrier gas inlet stream and the

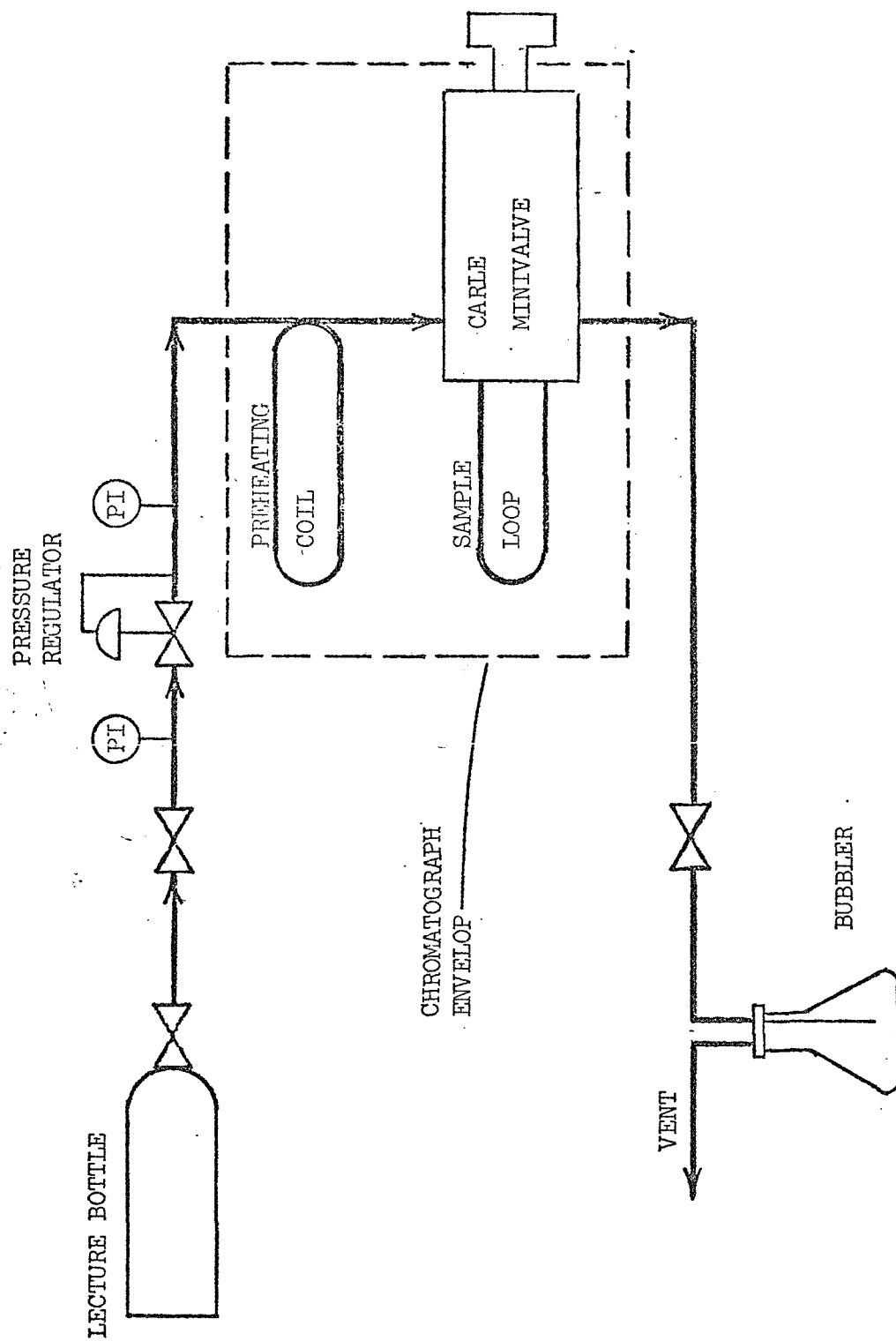
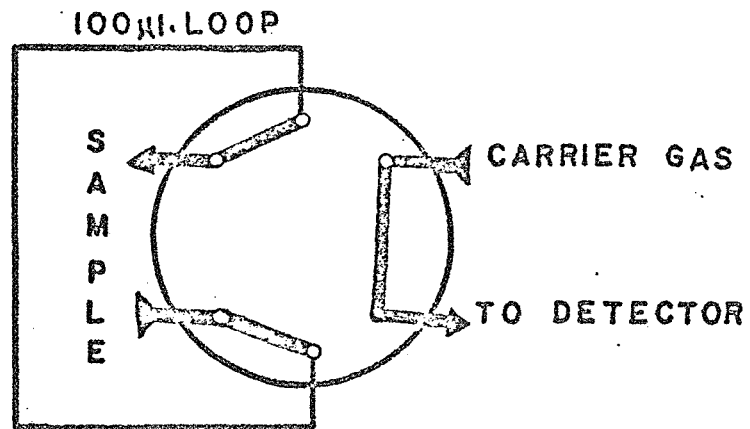


FIGURE 3. SAMPLE INJECTION SYSTEM USING CARLE MINI-VALVE

CARLE MINI-VALVE OPERATION

BEFORE INJECTION



AFTER INJECTION

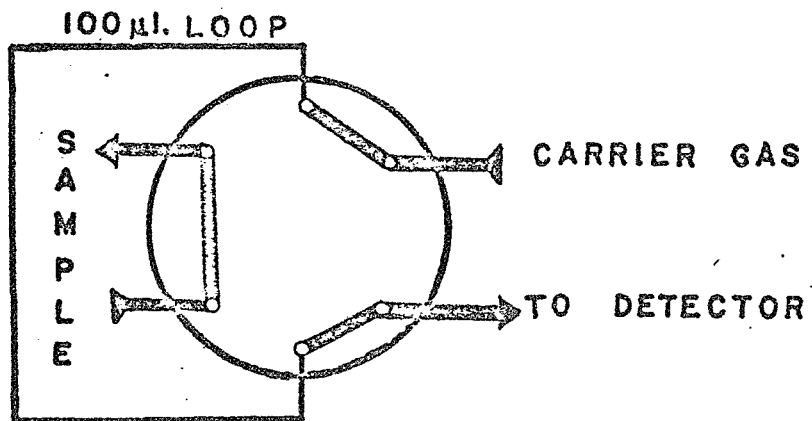


FIGURE 4

sample gas inlet stream are used to maintain the desired temperatures. An analysis of the preheaters using the Graetz heat transfer solution confirms the fact that the preheaters effectively maintain the gas at oven temperature.

From preliminary experiments, it is concluded that this system is capable of generating repeatable gas chromatograms which are suitable for comparing to the theoretical studies. The rapid response of the detectors and recorder to composition changes within the system indicate that the recorder output represents far more accurately the actual response of the system than could be obtained with commercial instruments.

In summary, the information obtained from the test facility consists of the following:

1. System input and output curves are recorded in arbitrary composition units as a function of time.
2. Flowrate, temperature, and pressure of the carrier gas are measured.
3. Column characteristics such as packing diameter and material, and column length and diameter are available.

This set of information is required for the evaluation of the mathematical models.

III. PARAMETER ESTIMATION

Given a gas chromatograph system that is capable of generating accurate, reproducible data, the next objective is to convert these data into the form used in the mathematical models for comparison purposes. The GC test facility presently being used will generate the following information:

1. An input curve, composition (in arbitrary units) vs. real time.
2. An output curve, composition (in arbitrary units) vs. real time.
3. Operating conditions: oven temperature, carrier gas flowrate and pressure, and detector signal attenuation.
4. Column information: length, diameter, packing mean diameter, packing void factor ϵ , and packing material.
5. Sample information: size of the sample and possibly sample pressure.

In addition, other physical property data such as densities, molecular diffusivities, and the like are available in the general literature. These data are further processed to compare the actual and predicted behavior.

The data reduction program was written to allow any of the models to be compared to actual system data. Although all mathematical models are functionally different, the models considered to date have common characteristics which have been incorporated into the program to simplify the calculations.

All the models define dimensionless time by the expression:

$$\theta = vt/L$$

where t is the real time in seconds, v is the gas velocity in cm/seconds, and L is the column length in cm. Therefore the composition vs. time curves, which are read into the program as finite data points with a constant time increment, Δt between data points, are converted in the program to dimensionless time data points with the interval between points being given by:

$$\Delta\theta = \Delta t v/L$$

Another characteristic of the models is that they all generate a dimensionless composition Y/A which has an area under the curve equal to unity. It is a characteristic of a gas chromatograph that the area under the output curve is directly proportional to the amount of sample injected. For example, if a sample of 21% oxygen and 79% nitrogen (air) is injected into a molecular sieve column, the output detector would record two distinct peaks. If the total area under both peaks is equal to unity, then under one peak will be 79% of the area which would correspond to nitrogen, and the other peak, oxygen, would have an area equal to 21%. This property would inherently create an error in our analysis if it was necessary to record exactly the sample size injected during each run. In addition, accurate detector calibrations would be required. These problems are eliminated by normalizing the input and output data so that they each have unit area. The data from the oscillograph is read into the computer in arbitrary units. The area under the curve is computed by numerical integration, and each data point is divided

by that area. The data are now in the form Y/A , as required by the mathematical models.

The models now being considered assume that the sample size is small compared to the amount of helium used, and that components act independently of each other. This assumption implies that the mathematical model may be solved for each component separately, and the solutions added linearly with an appropriate proportionality constant included. For example, if the oxygen-nitrogen system cited above is considered, the superposition assumption states that after the oxygen data is normalized to one, and the mathematical model may be solved for this case. Nitrogen may be solved in the same manner. The real solution is obtained by adding the oxygen and nitrogen models after multiplying each oxygen data point by 0.21 and each nitrogen point by 0.79. The same is done to the actual output data points and the two chromatograms may be statistically compared in this manner. The validity of this assumption is to be investigated during the next year.

The last similarity between the mathematical models is their common dependence upon the dimensionless parameter mR_0 . In the derivation of all the models (1), the term mR_0 represents the adsorption characteristics of a given component for the specific column packing being used. In essence, this quantity, to a 1st order approximation, determines when a particular component will elute from the column. The other dimensionless parameters,

P_e , a dimensionless parameter related to sample diffusion in the carrier gas

and

N_{tOG} , a dimensionless related to the approach to equilibrium
adsorption

both have a second order effect upon this 'retention time' of the component in the column. Since mR_0 will differ for each column packing used and each component used in the packing, this quantity is most easily calculated directly from the actual system data.

From previous work (1), an approximate value of mR_0 is given by:

$$mR_0 \sim 1/(\theta_{\max} - 1)$$

where θ_{\max} is defined as the theta value in the actual output at which the Y/A value is a maximum. In general, if a component elutes from a column in roughly a Gaussian curve, this θ value in real time is the 'retention time' for that component on the column packing being considered which is commonly cited in the literature. This equation for mR_0 was derived from the impulse response model of the system, and therefore does not include the effect of a finite input to the column. From experimental work it has been found that a better estimate of mR_0 is given by:

$$mR_0 \sim 1/(\theta_{\max} - \theta_{\max,i} - 1)$$

where $\theta_{\max,i}$ is defined as the dimensionless time at which the maximum of the input function appears.

The actual value of mR_0 is computed in the following manner for a particular set of data. The estimate of mR_0 is read into the program, and the output model is computer, using the compolution integral to be explained in the following section. The resulting value of θ_{\max}

is compared to the actual θ_{\max} of the data. If they differ, the value of mR_0 is adjusted using a first order iteration scheme. This procedure is repeated until the maxima of the two curves coincide.

Work was initiated this year into estimating mR_0 from heats of adsorption data given in the literature for specific gas chromatograph packings. Since mR_0 is a strong function of temperature, it has been shown (15, 16, 17, 18) that the effect of temperature upon the retention time of a component in a column may be estimated by:

$$t_{r2}/t_{r1} = \exp \left[q_{\text{ads}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) / R \right]$$

where

- T_1, T_2 = absolute temperatures
- t_{r1}, t_{r2} = retention times
- q_{ads} = heat of adsorption
- R = gas constant

This concept is a simplification of the processes involved but it does afford a means for correlating mR_0 data. This and other theoretical approximations of mR_0 will be studied in the coming year to evaluate their applicability to this project.

In the above manner data from a gas chromatographic experiment is reduced to a form to allow for direct comparison to the mathematical model being considered. Depending upon the form of the model considered, it is necessary to estimate P_e and N_{tOG} . The methods involved in estimating these dimensionless parameters are given in Section VI.

IV. NUMERICAL METHODS

In the course of the analysis on the computer, it is necessary to perform certain mathematical operations on the data. The accuracy of these numerical methods in turn affects the total accuracy of the data generated from the program. It is therefore necessary to investigate in some detail the numerical techniques used in order to estimate the magnitude of the system errors.

Because of the system complexity, the mathematical models derived earlier provide the impulse response of the system. However, in all chromatographs, sample injection requires a finite amount of time, so the impulse response introduces an error into the simulation. To account for finite pulse inputs, the system is assumed linear and the convolution integral (21) is used.

If the impulse response, $YP(\theta)$, of a system is known, and the system is linear, it is possible to calculate the system response for any input function $X(\theta)$ by one of the following integrals:

$$\begin{aligned} \text{Output } (\theta) &= \int_{-\infty}^{\theta} X(\lambda) YP(\theta - \lambda) d\lambda \\ &= \int_{-\infty}^{\theta} YP(\lambda) X(\theta - \lambda) d\lambda \end{aligned}$$

This is sometimes called the convolution, Carson, or Faltung integral.

In this case, since the input function is applied at zero time, the lower limit is adjusted to zero without losing any generality. It should be

noted that the two integrals shown are completely equivalent and either may be used in a given situation. This fact will be used in our application of the integral. It is assumed that both $YP(\theta)$ and $X(\theta)$ satisfy the Dirichlet conditions over the interval $(0, \theta)$ so step functions and other discontinuous inputs may be handled.

For use on the computer, the integration is performed digitally with a finite number of data points. In the computation, the integrand is represented by the following discrete form:

$$\text{Integrand} = X(\lambda) YP(i - \lambda + 1) \quad \lambda = 1, i$$

where $YP(i)$ = impulse response

$X(i)$ = input function

This expression may be explained in the following manner. The input function is read into the program so that $X(i)$ represents the curve in array form. In general, the sample is finite and is injected in a finite length of time which is designated by the index M . Hence, all values of the input function $X(i)$ for $i \geq M$ are set equal to zero. The impulse response, which is computed from the particular system model being considered, is placed into the array $YP(i)$.

The integrand is then computed as a set of numbered pairs shown schematically in Figure 5. Then the area, which is the system output for the given input function, is estimated numerically using Simpson's method and is reported as the output vector $\phi UT(i)$. When i is odd, Simpson's method is used directly, but if i is even, the terms from $\lambda = 1$ to $\lambda = i-1$ are integrated using Simpson's rule, and the last two data points are integrated using the trapezoidal rule (19):

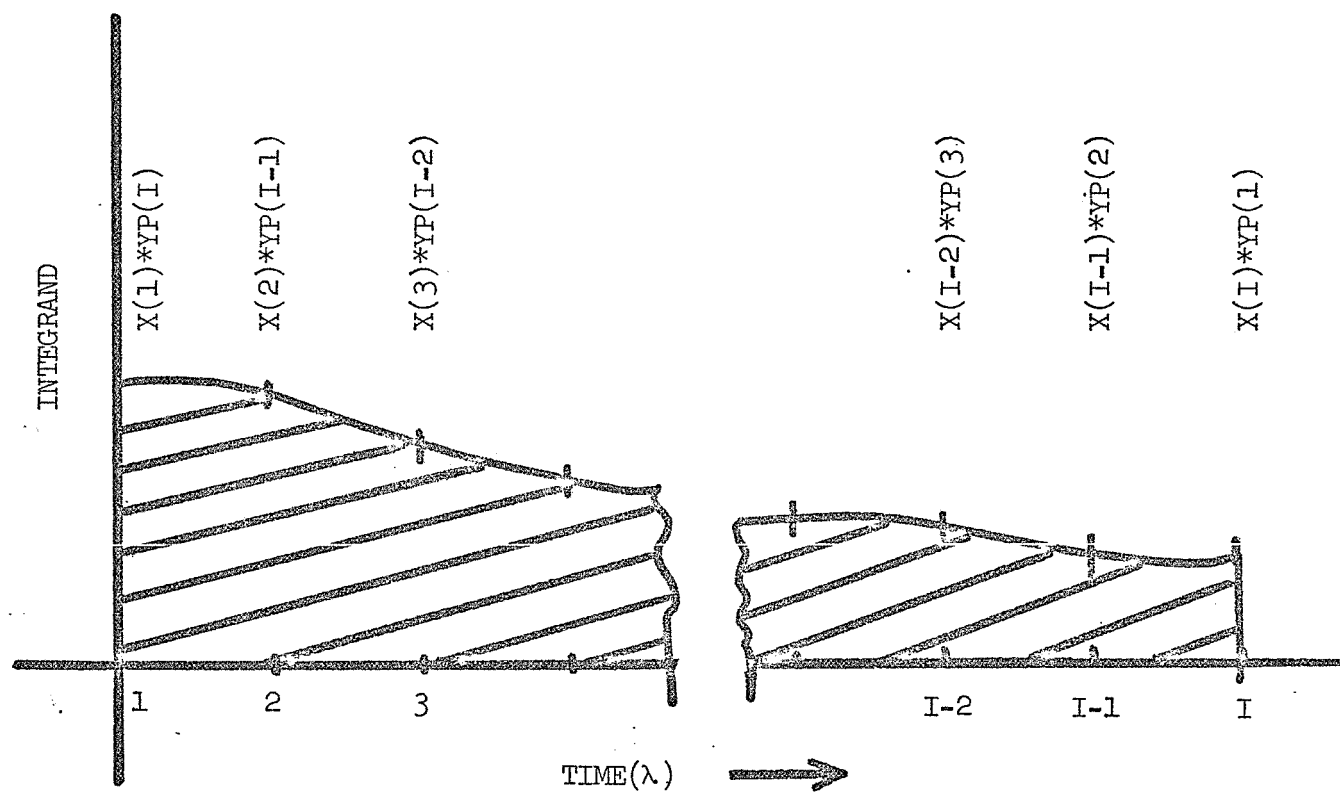


Figure 5. Digital Representation of Convolution Integrand

$$\text{Area} = [X(i-1) YP(2) + X(i) YP(1)] / 2$$

This area is added to that found for the other data points by Simpson's method to yield the value of $\phi_{UT}(i)$.

By looking at the digital form of the integral, it is possible to avoid much needless integration of data points having values of zero. This is done in the following manner. The input function contains non-zero data points for time elements in the range $i = 1, M-1$; and the first zero data point occurs at the time corresponding to $i = M$. Because subsequent values of $X(i)$ are set equal to zero (the sample injection being completed), it is only necessary to evaluate the integral for $\phi_{UT}(i)$ in the range $\lambda = 1, M$. For all values of M , the ordered pair $X(\lambda) YP(i-\lambda+1)$ will be zero. This is shown schematically in Figure 6. The convolution subroutine, designated $C\phi_{NV}$ in the computer program, performs the integration for $\phi_{UT}(i)$ according to this strategy. This results in a considerable saving in computer time in some cases. For example, if the mechanical injection valve is used for introducing the sample, injection is usually completed within 1.5 seconds. If the data points required to represent the input function are separated by 0.1 second, the value of M in this case is 15.

If ethylene is injected in this manner at room temperature, the data in Section VI shows that it will take 1500 data points to describe the output curve for a Chromasorb 102 column. In other words, the last detectable amount of sample eluted from the column was approximately 147.5 seconds after the initial injection of the sample. For values of $\phi_{UT}(i)$ where $i > 15$ the program will form only the first 15 data points and integrate under this curve. At a time approaching the end of the

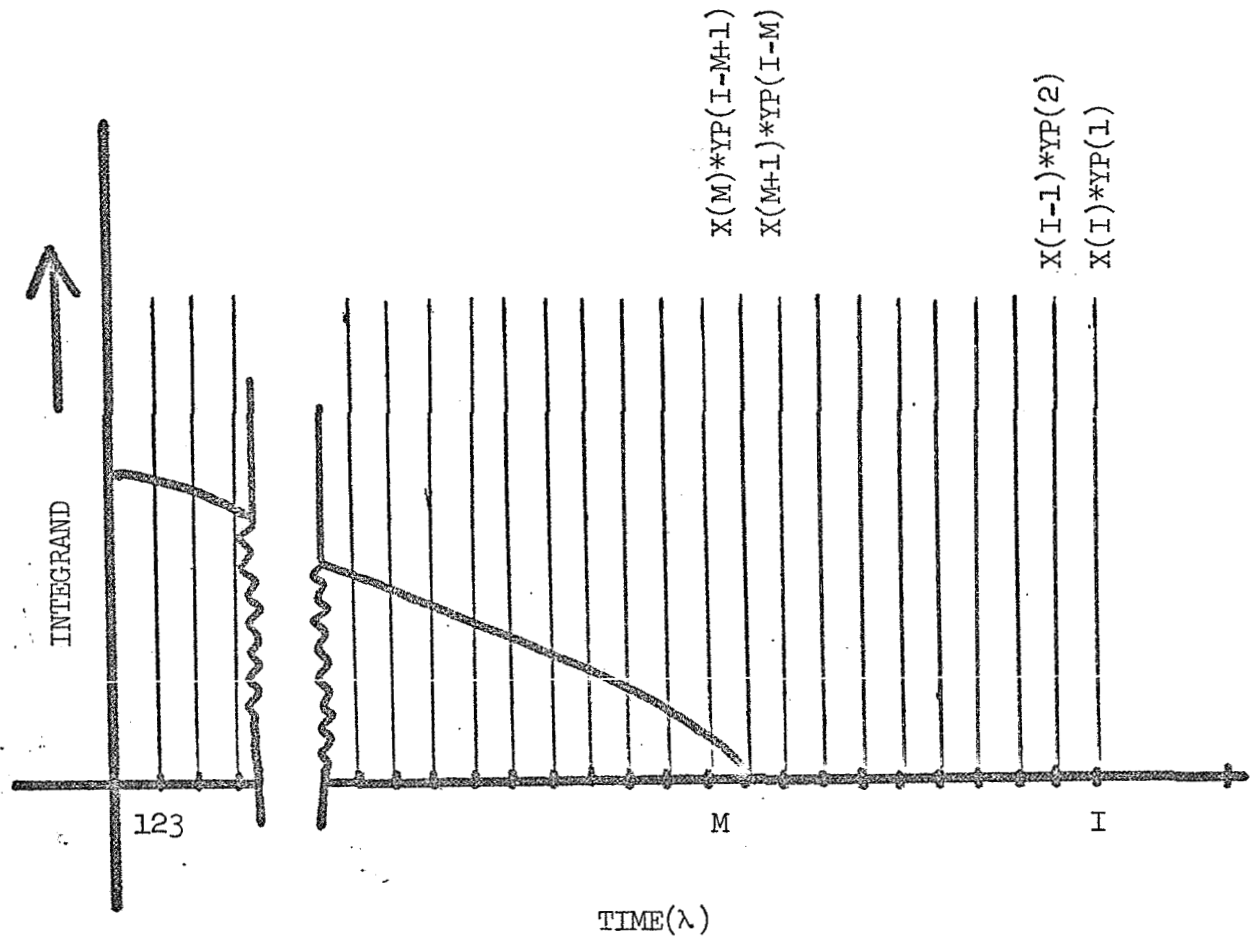


Figure 6 Integration Cut-Off Technique

chromatogram, say at 140 seconds ($i = 1400$) the subroutine would be computing the area under 1385 zeros unnecessarily if the program simply formed all of the data pairs. Thus a considerable saving of computer time is possible.

To reduce the effects of sample injection size and differences between the calibrations of the two composition detectors upon data analysis, the areas under the input and output curves are each normalized to unity. Because the impulse response from the theoretical model is also normalized to unity, this procedure is equivalent to imposing a material balance on the sample, and insures that the input and output data are quantitatively consistent.

This normalization is done automatically in the DATAJT subroutine. The subroutine is given the input and output arrays from the main program. The areas under these curves are calculated using the QSF subroutine (26) which employs a modified Simpson's method. Then the data points in each array are divided by the calculated area to normalize the array. Under these conditions, the area under the convoluted output curve, which is derived from normalized data, should be near unity.

If the area under the convoluted curve differs appreciably from unity, the function integrated was too peaked and more data points must be included to obtain a better integration.

All integrations in the data reduction program use Simpson's method (19,20). The general definition of this integration scheme is as follows:

Let f_1 through f_n define a set of data points, where n is odd. If the spacing between data points is given by H , then the area under the points is given by:

$$\int_{x_0}^{x_0+nH} f dx = H/3(f_1 + 4f_2 + 2f_3 + 4f_4 \dots + 2f_{n-2} + 4f_{n-1} + f_n)$$

This method was chosen because it is an excellent numerical approximation when considering a set of fixed data points. The approximate error in this method is of the order of $H^5(20)$.

This integration method works well for smooth curves with no major discontinuities. However, if the number of data points is small, and the curve is peaked, errors in the method increase. It is therefore necessary, when inputting data to the program, to be certain that the interval H is small enough so that a reasonable number of data points appear. This is especially true when the mechanical valve is used for injection. In this case, as noted before, the entire injection generally takes place within about 1.5 seconds. A value of H must be chosen to give at least 10 data points for the integration. Therefore an interval of 0.1 second is usually chosen.

Of the parameter in the theoretical models, only the thermodynamic parameter mR_0 is not predictable a priori and it must be determined from the experimental data. This parameter mR_0 primarily affects the time at which the maximum composition appears in the output chromatogram. Hence a curve-fitting procedure is used which positions the maximum point of the convolved output exactly at the time when the maximum concentration appears in the experimental data. Exact matching is possible because in the computations, time is considered in discrete intervals and is represented as an integer.

Determination of mR_0 requires the solution of a nonlinear equation, so a first-order, iterative process, the regula false method (19,20) is

used. Starting with an initial estimate

$$mR_0 = 1/(\theta_{\max, \text{out}} - \theta_{\max, \text{in}} - 1)$$

the technique proceeds as shown in Figure 7. The appearance time for the maximum composition in the data is designated as T_{\max} . Proceeding from the initial estimate mR_0 , two new estimates mR_0' and mR_{01} are found, one being 10% larger than the initial estimate, the other being 10% smaller than the initial estimate. The impulse responses for these two values of mR_0 are computed, and are convoluted with the output data. The maxima of each generated curve are bound to occur at T_{\max} , and T_{\max_1} respectively as is shown in the diagram. The false position method predicts a better estimate of mR_0 , designated as mR_{02} as follows:

$$mR_{02} = mR_{01} - (T_{\max_1} - T_{\max})(mR_{01} - mR_0') / (T_{\max_1} - T_{\max}')$$

The procedure is repeated, but now the terms in the above equation, mR_{01} and T_{\max_1} are replaced by mR_{02} and T_{\max_2} respectively in the next estimate of mR_0 . This procedure is repeated until the value T_{\max_1} is equal to T_{\max} .

It should be noted that this method will converge only when the initial estimates mR_0' and mR_{01} are sufficiently close to the time value. If they are not, the iteration may diverge. The point (mR_0', T_{\max}) is held constant and considered the reference point for the iteration. In some other iteration methods this base value is also varied, but in this case this was found to be unnecessary. It typically will take six to eight estimates before the actual value of mR_0 is

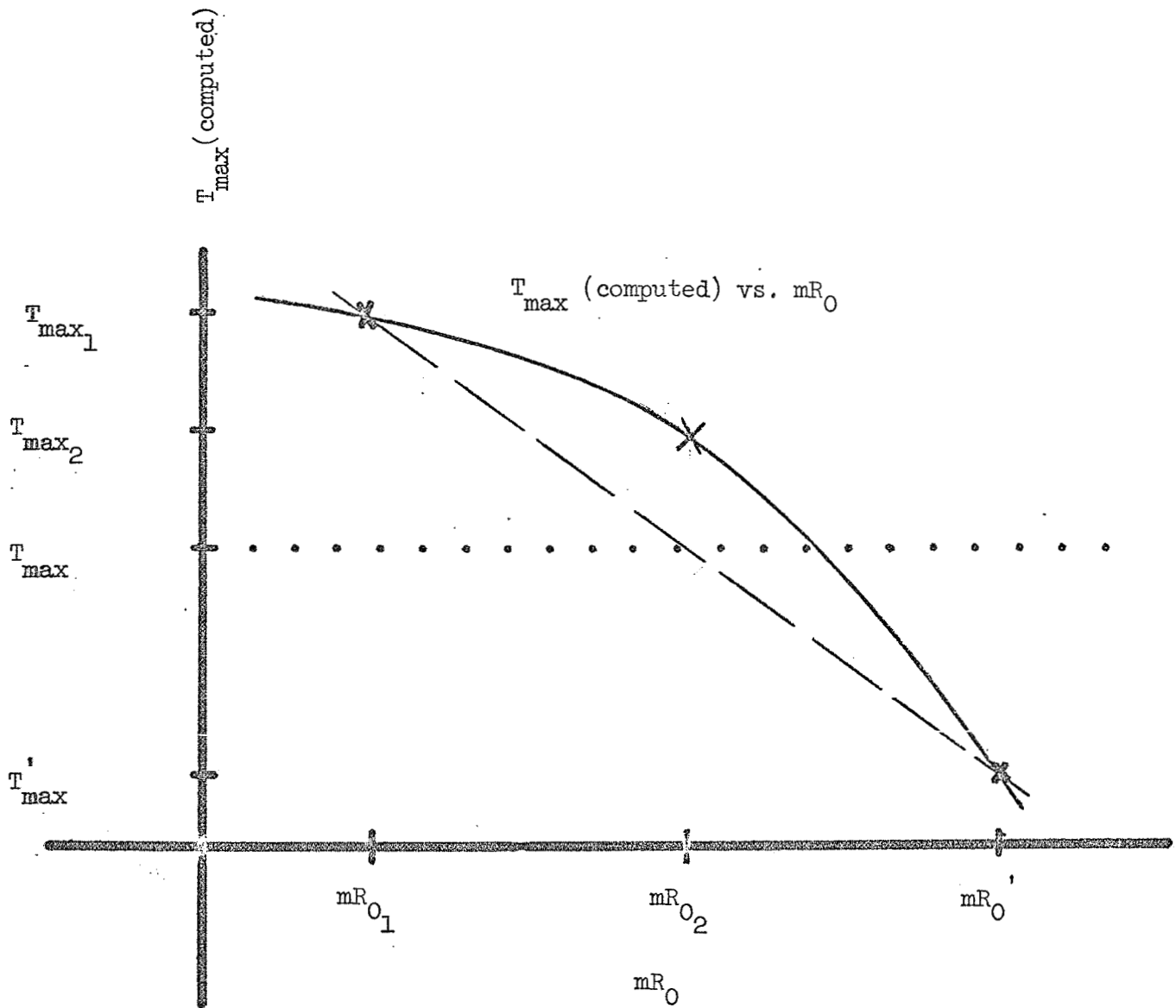


Figure 7. Regula-Falsi Iteration for mR_0

obtained. If the procedure does not converge after the maximum number of iterations in the program (20), the last value of mR_0 computed is printed out. The procedure can be repeated as a new set of calculations, if necessary, using the final value of mR_0 as the initial estimate. In general this is not necessary. Table I compares the actual value of mR_0 with the value computed in the regula false routine. The number of iterations for convergence are also given for two systems - acetone and ethylene at various temperatures.

The statistical data computed in the program is done using the TALLY subroutine (27). This subroutine will compute the standard deviation, maximum average values of the impulse function, convolved output, and the actual system data using standard computing equations (22).

The last scientific subroutine used is RPLOT (see Appendix A). It is a local program developed at Rensselaer that is capable of plotting data in polar, logarithmic, semi-log spherical or rectangular coordinates. It is also capable of plotting up to 33 sets of data on the same graph. In the data reduction program, RPLOT is used in several ways. First the input function Y/A is plotted against the dimensionless time θ . This is done by moving data points from the array $X(i)$ into the RPLOT storage array $YY(i,j)$. The first index of YY designates the i^{th} data point of the array to be plotted. The second index tells the subroutine which array is being plotted. With this program it is possible to plot up to 33 separate arrays on the same graph. Therefore j may take on a value of 1 to 33. The corresponding value of the dimensionless time $\theta(i)$ is also moved into the RPLOT storage array $TT(i,j)$ in a similar manner.

TABLE I

mR₀ Iteration Information

<u>Temperature</u> <u>°C</u>	<u>mR₀,</u> <u>Initial</u>	<u>mR₀,</u> <u>Final</u>	<u>Number of</u> <u>Iterations</u>
---------------------------------	--	--	---------------------------------------

Ethylene System

20	0.0858	0.0858	1
50	0.1316	0.1322	3
75	0.2008	0.2009	2
100	0.2420	0.2435	4
125	0.2535	0.2545	3
150	0.2900	0.2939	6

Acetone System

100	0.2240	0.2232	2
125	0.4580	0.4600	3
150	1.144	1.098	6
175	1.715	1.594	17

After plotting the input function, RPLOT now plots the impulse response, convolved response and actual response on one graph. For this operation the program uses the information from the digital printout of the data. The first non-zero and the last non-zero data point of the three output arrays have been found previously. These values are used as the limits of the data points to be plotted. This eliminates the plotting of many zeros in the output and allows for a much better visual representation of the data. The methods are similar to those used in plotting the input function, only in this case the impulse response $YP(i)$ is moved to $YY(i,1)$, the convolved response $\phi UT(i)$ goes to $YY(i,2)$ and the actual data array $YDATA(i)$ is moved to $YY(i,3)$. The corresponding values of the dimensionless times are also moved to $TT(i,1)$, $TT(i,2)$ and $TT(i,3)$.

Lastly, it has been found that since the impulse response is in general much more peaked than the actual convolved response, the plotting of all three arrays occasionally has the effect of causing the actual data and the convolved data to fall almost on the same curve, thereby eliminating a visual comparison. The program therefore plots the convolved and actual data on a separate graph for accurate comparison of the model to the real system response. The methods employed are analogous to the approach used in plotting the three arrays together.

In using RPLOT it is necessary to input to the storage arrays one hundred data points or less. The program therefore scans the array to be plotted, and if the number of data points is greater than one hundred, it systematically skips data points until the number is under one hundred. For example if the number of points to be plotted is 321, the program first tries to use all the points. Next it will skip every

other data point - which would give 160, still too large. Next it would skip two data points before recording the third. This would give 107, which is still too large. Finally it would skip three data points. For this case 80 data points would be plotted. This is necessary to avoid an overflow in the RPLOT subroutine.

V. DATA REDUCTION PROGRAM

The data reduction program was written in FORTRAN IV language for the IBM 360/50 computer. It is composed of a main calling program and six subroutines:

- DATAJT - program for normalizing input and output data
- QSF - library supplied integration program (26)
- C~~O~~NV - numerical convolution procedure
- TALLY - library supplied statistical program (27)
- RESP - mathematical model being considered
- RPPL~~O~~T - data plotting program

A complete listing of the program is given in Appendix A followed by a definition of all program variables, the flow diagram, and the method of data input for operation. In this section the program will be explained in general terms and the more important system parameters and array names will be given to help the reader follow the program listing. The overall system procedure is summarized in Table II.

After the system storage arrays have been dimensioned, and all counters have been initialized, all program data is read into memory. The first card to be read in is a general Hollerith data card for the output title. Whatever is written on this card is printed out at the top of the first output listing page, and at the bottom of the comparative plots for the data and model. In general, one would put on this card the system being considered, the temperature, column packing, flowrate of helium, etc. to define the system being analyzed.

Next certain counters to be used in the program are read in, after which the input data is read in under the name X(M). After reading in

TABLE II

Outline of Data Reduction Computer Program

1. Read in all data.
2. Normalize input and output data.
3. Calculate optimum value of mR_0 using impulse response, convolution integral, and regula falsi iteration.
4. Print out all input and output curves.
5. Calculate statistical data.
6. Plot out generated curves.

M data points, the program automatically assigns zero to all subsequent values of $X(I)$. This is necessary for evaluating the convolution integral, as explained previously. It should be noted here that $X(1)$ corresponds to $\theta = 0$, and any following value of $X(K)$ corresponds to $\Delta\theta \cdot (K-1)$. In other words the output at $\theta = \Delta\theta \cdot (K-1)$ is equal to $X(K)$, $K = 1, N$. All arrays used in this program follow the above nomenclature. The system parameters are read in next. These include mR_0 called ROM, the Peclet Number, PE, and column length, ALENG and velocity, V, the number of theta increments to be considered, N, and finally the theta spacing, $\Delta\theta$, called H. The variable N is defined in the following manner. If the last data point from the output data is read in at $\theta = Q$, then the number theta increments necessary to define the system is

$$\text{number of increments} = Q/H$$

This represents the minimum usable value for N. In general, N is made approximately 50 greater than this number so all of the simulated output will be included. It should be noted that the program requires the input and output data to have the same theta spacing H. This can lead to problems if for example, the Carle injection valve is used, in which the sample is injected into the column in approximately 1.5 second. The output curve for the system might be 30 seconds long. To define the input function correctly a time spacing of 0.1 second would be appropriate. This would require 300 data points be read in to define the output curve since the same spacing must be used. The result is a large number of data cards for the output data. As an additional point, the maximum value of N is 1500 due to the limitations in storage in

the computer. It is therefore necessary to choose a value of $\Delta\theta$ so that the maximum theta value obtained in the program is less than $1500 \cdot \Delta\theta$.

Finally the output data is read into memory in the following manner. Since the output will be zero for a specified time until the component begins to elute, this time is read into the program as a number of delta the spacings, called K_1 ,

$$K_1 = T/H$$

where T is the theta time when the component first begins to exit the column. The output array, $YDATA(i)$ is set equal to zero for $i < K_1$. The output curve is then read in and all values between the last data point and the last data array element (having index N) are set equal to zero. This means if it takes 250 theta points to define the output curve, and N was set to 300, all values of $YDATA(i)$ for $250 < i \leq 300$ will be set equal to zero.

The input and output curves are now normalized so that the area under each curve is equal to one using the DATAJT subroutine. The areas are determined by the subroutine QSF. Each data point is divided by the appropriate area in the normalizing procedure DATAJT.

The programs then begins to calculate the simulated output chromatogram. The assumed value of mR_0 is transferred into the subroutine RESP which contains the mathematical model to be considered. An impulse response curve, $YP(i)$ is calculated. This response curve is then convolved with the input function to yield a response which accounts for the sample injection. The digital methods employed in the convolution subroutine (CONV) were considered in the previous section.

The theta value of the maximum Y/A value of the simulated output is found and compared to the maximum of the actual output. If they differ, the value of mR_0 is adjusted using the regula-false 1st order iteration scheme. This procedure is followed until the maximum points of the two curves are identical, or until 20 iterations have been performed. After 20 iterations, the final value of ROM is used.

The program now prints out the original data card listing the description of the system on a new page. It follows this with the system parameters such as the 11 column length and gas stream velocity, etc. It now prints out headings and the total input data including the value of theta, the actual time in seconds, the output array OUT(I), the actual data YDATA(I), and the impulse response YP(I). After printing out the entire input function, the program indexes until the first non-zero data point in any of the output curves, OUT, YP, and YDATA, is obtained. Then all the output are printed out until the last non-zero value of any of the three arrays is reached.

Statistical data concerning the curves are now computed by the subroutines TALLY and QSF and are printed out. These include the standard deviation, average value and maximum of each of the three output arrays. The input function with appropriate headings is plotted out using RPLOT subroutine. Next the three output chromatograms are plotted out on a single graph also using RPLOT with headings included. Finally the convolved output is graphically compared to the actual system data using RPLOT.

VI. RESULTS AND DISCUSSION

To run the data reduction program, a mathematical model must be chosen. This model must predict the chemical separation which occurs in flow through a packed bed. The simplified theoretical model is depicted in Figure 8. A carrier gas plus sample is flowing through a packed column in such a manner that the sample is dispersed axially by turbulent and molecular diffusion around the packing. This process is characterized by the dimensionless Peclet number P_e . Radially the sample is also transported by turbulent diffusion and by the adsorption and desorption at the packing surface. The rate of this adsorption-desorption process is governed by the behavior of the carrier gas in the vicinity of the particle represented by the dimensionless parameter N_{tOG} the number of transfer units, and by the characteristics of the particular adsorbent phase being used in the column. This adsorbent phase is characterized by the thermodynamic parameter mR_0 .

This simplified approach is based on certain assumptions. First the column is assumed to operate isothermally, which basically holds constant the rate of adsorption and desorption within the column. Secondly, the velocity profile is flat, which allows the use of a mean velocity in the column which is independent of radius. It is assumed that the gas composition is approximately constant in the direction normal to flow, and the concentration gradient occurs only in a thin boundary layer near the adsorbent. With this assumption mass transfer coefficients or the parameter N_{tOG} may be introduced. The adsorbent layer is assumed to be so thin that there is no diffusion within the layer, and that there is no diffusion through the solid phase of the packing material. The

CHROMATOGRAPHIC COLUMN CONCEPTS

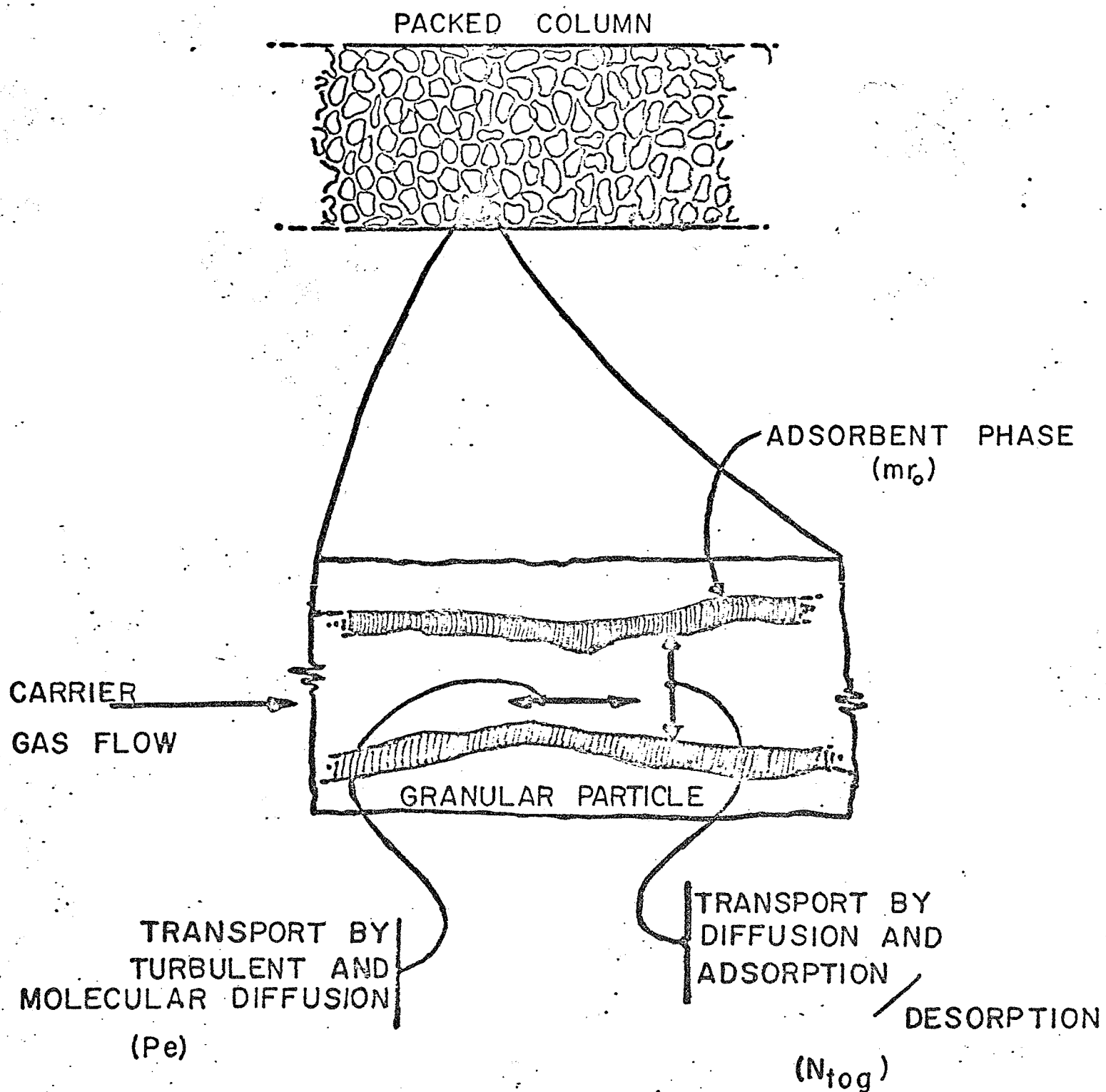


FIGURE 8

carrier gas is assumed to have a negligible rate of adsorption, and to behave as an ideal gas. Finally the concentrations of the sample components are assumed to be very small at any point in the column.

With these assumptions it is possible to derive a set of dimensionless differential flow equations for the system (1). For the present study, as a means of evaluating the data reduction program, and also to do some preliminary evaluation of system data, the equilibrium adsorption model described in the introduction was chosen. This model only includes the effects of axial dispersion (P_e) and the rate of adsorption (mR_0). For this model, it is assumed that at any point in the column, the gas phase of any component in the sample is in equilibrium with the adsorbed phase on the column packing, that is, the number of transfer units, N_{tOG} , is infinitely large. In general this assumption is valid if the L/D ratio of the column is large. For use on Mars, several proposed column designs are well within this limitation (28).

This particular model was chosen because it is a closed form solution and is easily adaptable to computer computation. Also, if the model proves to describe adequately the data, its solution for many sample cases is much easier than a more complicated solution which includes the effects of N_{tOG} (7).

The Peclet number must be estimated if this model is used. As mentioned earlier, the Peclet number takes into account the axial dispersion of the sample as it passes through the column. As an example, consider Figure 9. This shows the chromatograms of ethylene was injected into a 60-80 mesh, glass bead column. Since the glass beads have no adsorptive characteristics, the only effect observed is the axial

COLUMN DISPERSION CHARACTERISTICS

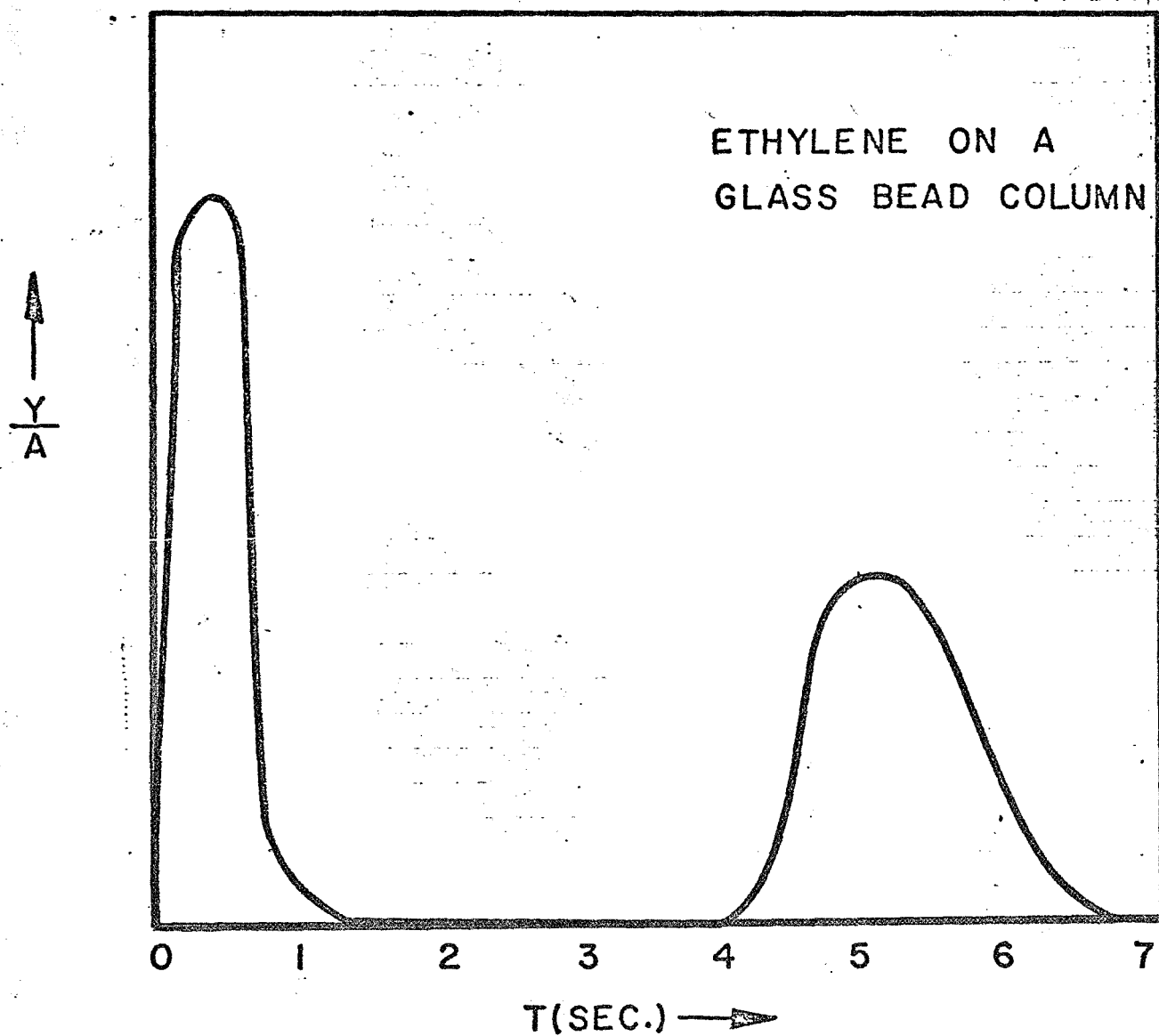


FIGURE 9

dispersion of the gas sample as it passes through the column. The gas was injected by the Carle injection valve, in pulse form. But as is shown, the maximum concentration of the sample is reduced by about 50% by the dispersion in the column. Ideally, if there were no dispersion of the sample, the sample pulse would appear at the end of the column with no loss in maximum concentration. From these data, it is evident that the dispersion effects in a packed column are not negligible, and for any model to accurately describe the physical situation at hand, it must include a term that will account for the dispersion of the sample as it passes through the column.

It has been shown (23), that it is possible to estimate the Peclet number by a correlation with the dimensionless group

$$\text{Re} \cdot \text{Sc} = d_p v / D_{AB}$$

where:

d_p = mean packing diameter

v = mean gas velocity

D_{AB} = molecular diffusivity of a component A into carrier gas B.

This group is a product of the dimensionless Reynolds number (Re) which characterizes the fluid mechanics of the system and the dimensionless Schmidt number (Sc) which is related to the molecular properties of the system. The diffusivity D_{AB} is computed for a given component using a known correlation (29). A sample calculation of the mean gas velocity and the molecular diffusivity is given in Ref. (30). A correlation of $\text{Re} \cdot \text{Sc}$ to Pe is shown in Figure 10 (23). For the Peclet number equal to infinity, there is no axial dispersion. It is seen from the

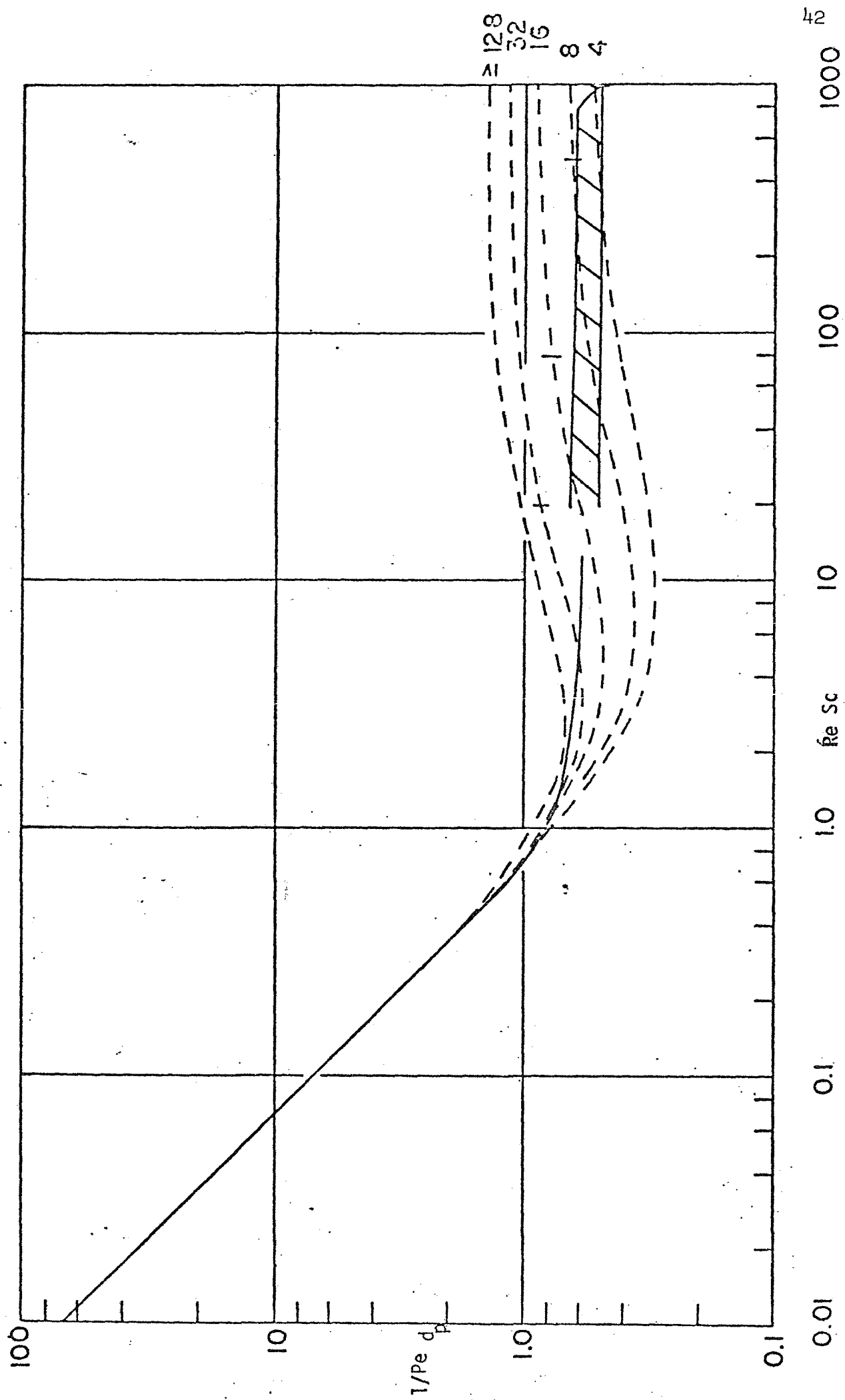


FIGURE 10

figure, that the gas flow rate and the particle diameter are the major factors which influence the Peclet number. The diffusivities of most gas systems are about the same, within an order of magnitude.

Since the Peclet number is so important in the mathematical simulation of a gas chromatograph, it will be necessary to insure that it is estimated accurately. The cited correlation is somewhat questionable, and more work is planned in this area. One possible method of estimating Pe directly from the data is as follows. If mR_0 is set equal to infinity in the equilibrium adsorption model, the model predicts that there is no adsorption of the sample onto the column packing. Sample runs for this case are available, such as those shown in Figure 9. By statistically fitting the equilibrium model to the actual data by varying the Peclet number, it would be possible to accurately estimate the Pe for that specific run. This information could be then utilized in analysis of the correlations. It would also be possible to form a Pe correlation plot for a specific packed column by varying $Re \cdot Sc$ and for each run fitting the model to the data and arriving at the 'optimum' Pe number for each value of $Re \cdot Sc$. These ideas are being considered for future work.

If other system models are considered, it will be necessary to determine N_{tOG} . It is therefore helpful to review the correlation involved in estimating this parameter. N_{tOG} is defined as (27):

$$N_{tOG} = Sh \cdot a \cdot L / Re \cdot Sc$$

where a = the packing surface area per unit volume

L = the column length

Sh = the Sherwood number

$$= Sh_0 + .347(Re \cdot Sc)^{.62}$$

At isothermal conditions Sh_0 is constant at about 2.00, and since the product $Re \cdot Sc$ which was considered earlier is known, all of the terms are easily calculated. Qualitatively, N_{tOG} indicates how close the system is to an equilibrium state at any point in the column. As N_{tOG} approaches infinity, the gas phase approaches an equilibrium with the solid or liquid packing phase.

Using the given estimate of Pe , the data reduction program was run using the equilibrium adsorption model. Initial studies as summarized in Table III centered around samples of air, isobutane, ethylene and acetone at various flowrates. These data are given in Figure 11. For each run the input curve is given in dimensionless time (θ) and comparative plots of the impulse response, the convolved response, and actual system data are plotted on one graph. In certain cases, a final comparative plot of only the convolved or simulated response versus the actual data is given to show better the differences between the two outputs. Pertinent information concerning the column packing, helium flowrate, and temperature are given with the plots and in Table III. All these graphs were generated by the RPPILOT subroutine.

The first two sets of data given, namely for isobutane, and ethylene were obtained using the Carle injection valve. The convolved output therefore differs only slightly from the impulse response, and as a first approximation the impulse response could be used directly. Since in both cases the dispersion in the sample is underestimated, it appears that the parameters of the model must be revised or that the model fails to account for some transport mechanism taking place. Prior work (6) has shown that the thermodynamic parameter mR_0 strongly influences the time at which the chromatogram peak occurs, but has little effect

TABLE III

Experimental Conditions for Initial Studies

<u>Component</u>	<u>Column</u> *	<u>Helium Flowrate</u>	<u>Temperature Range</u>	<u>Data Reference</u>
Isobutane	Chromasorb 102	38 ml/min	20°C	Fig. 11
Ethylene	Chromasorb 102	38 ml/min	20°C	Fig. 11
Nitrogen	Molecular Sieve, 5A	35 ml/min	20°C	Fig. 11
Oxygen	Molecular Sieve, 5A	35 ml/min	20°C	Fig. 11
Acetone	Chromasorb 102	24 ml/min	125°C	Fig. 11
Acetone	Chromasorb 102	43 ml/min	100-200°C	Fig. 12
Ethylene	Chromasorb 102	43 ml/min	28-175°C	Fig. 13

* Physical constants for all columns: length - 1 meter, inside diameter - 2.2mm, particle size - 60/80 mesh (0.250/0.177 mm.).

Figure 11

Preliminary Results Using Various Injection Techniques

- a,b Isobutane on Chromasorb 102. Input and Chromatograms.
- c,d Ethylene on Chromasorb 102. Input and Chromatograms.
- e,f,g Nitrogen on Molecular Sieve. Input and Chromatograms.
- h,i,j Oxygen on Molecular Sieve. Input and Chromatograms.
- k,l,m Acetone on Chromasorb 102. Input and Chromatograms.

PLCT CF SYSTEM RESPONSE 0=IMPULSE RESPONSE, 1= CONVOLVED RESPONSE TO INPI, I FUNCTION

3.6CE CC

3.2CE CC

2.8CE CC

2.4CE CC

2.0CE CC

1.6CE CC

1.2CE CC

0.8CE-01

4.0CE-01

C.CCE-01

-4.CCE-01

7.CCE CC 7.20E 00 7.40E 00 7.60E 00 7.80E CC 8.CCE CC 8.2CE CC 8.4CE CC 8.6CE CC 8.8CF 00 9.00E 00

THIS IS A PLCT CF Y/A VS. DIMENSIONLESS TIME FOR M RO= C.146591 AND A PECLET NUMBER= 7200.000000

ISOBUTANE ON A CHRCVACRB 102 CCLUM, 38 CC/MIN., 20 DEGREES CENTIGRADE

כ.כ.

1. CCE CC

THIS IS A PLOT OF γ/α VS. DIMENSIONLESS TIME FOR $M_{\infty} = C_{172C14}$ AND A PECLET NUMBER = 6700.00000

PLCT CF SYSTEM RESPONSE 0=IMPULSE RESPONSE, 1= CONVOLVED RESPONSE TO INPUT FUNCTION
2=ACTUAL DATA FROM GAS CHROMATOGRAPH

[illegible]

3.2CF CC

2.803 CC

2.4CE CC

2, 3, 4, 5

1.43E CC

1.2CE.CC.

10-333 E

4, CCE-01

C. CCE-CL.

	6,50E 00	7,00E 00	8,00E 00	9,50E 00	1,00E 01	1,10E 01
6.CCE CC	7.50E 00	8.00E 00	8.50E 00	9.00E 00	9.50E 00	1.00E 01

THIS IS A FLCT CF Y/A VS. DIMENSIONLESS TIME FOR M RO= C.172C14 AND A PECLET NUMBER= 67C0.0C0000

ETHYLENE ON A CHROMASORB 102 COLUMN, 38 CC/MIN., 20 DEGREES CENTIGRADE

PLOT OF THE INPUT FUNCTION

5.C

4.5CE CC

4.CCE CC

3.5CE CC

3.CCE CC

2.5CE CC

2.CCE CC

1.5CE CC

1.CCE CC

5.CCE-01

C.CCE-01

C.CCE-01 8.COF-02 1.60E-01 2.40E-01 3.20E-01 4.CCE-01 4.8CE-01 5.6CE-01 6.4CE-01 7.2CE-01 8.00E-01

THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR N RO= C.8C41E9 AND A PECLEY NUMBER= 6.691.199000

53

THIS IS A FLCT CF Y/A VS. DIMENSIONLESS TIME FOR M KO= C.8C41E9 AND A PECLET NUMBER= 6691.199000

[illegible]

1.2CE CC	1.3CE CC	1.40E 00	1.50E 00	1.6CE CC	1.7CE CC	1.8CE CC	1.9CE CC	2.0CE CC	2.10E 00	2.20E 00
----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

THIS IS A FLCT CF Y/A VS. DIMENSIONLESS TIME FOR M RO= 2.2215E7 AND A PECLET NUMBER= 6691.190000

OXYGEN ON A MOLECULAR SIEVE COLUMN, 35MCC/IN., 20 DEGREES CENTIGRADE

PLCT CF SYSTEM RESPONSE 0=IMPULSE RESPONSE, 1= CONVOLVED RESPONSE 1C INPLT FUNCTION

1.8CE CC

1.6CE CC

1.4CE CC

1.2CE CC

1.0CE CC

8.CCE-Cl

6.CCE-Cl

4.CCE-Cl

2.CCE-Cl

C.CCE-Cl

-2.CCE-Cl

8.CCE CC 1.00E 01 1.20E 01 1.40E 01 1.60E 01 1.8CE Cl 2.CCE Cl 2.2CE Cl 2.40F Cl 2.60E 01 2.80F 01

THIS IS A PLCT CF Y/A VS. DIMENSIONLESS TIME FOR M RO= C.C776E2 AND A PECLT NUMBER= 5750.000000

ACETONE ON A CHKCNASRB 102 CCLMNA, 24 CC/MIN., 125 DEGREES CENTIGRADE

[illegible]

E.CCE CC	1.0CE 01	1.20E 01	1.60E 01	1.8CE 01	2.0CE 01	2.2CF 01	2.4CE 01	2.6DE 01	2.8OE 01
----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

THIS IS A PLCT CF Y/A VS. DIMENSIONLESS TIME FOR M RD= C.077682 AND A PECLET NUMBER= 5750.000000

ACETOXY ON A CHROMASORB 102 COLUMN, 24 CC/MIN., 125 DEGREES CENTIGRADE

upon dispersion. On the other hand, the Peclet number strongly affects dispersion (6) so perhaps the estimate of Pe was in error as noted above.

As a second system to consider, air was injected into a molecular sieve column using a syringe. These results are also shown in Figure 11. Oxygen and nitrogen components were treated as acting independently and the results are given in this manner. The θ vs. Y/A plot for the input function is also given for this case. As before, the dispersion in the sample is not exactly predicted by the equilibrium model, although for this set of data the model approximates the data better than for ethylene and isobutane. If the errors in estimating Pe are about the same, this suggests that the model is too simple.

The last system used in the preliminary studies was acetone with a porous polymer adsorbent. This sample was injected by a syringe and vaporized in the injection block chamber. The comparative plot and the input function are also given in Figure 11. Again the extent of dispersion is not predicted, although the error is between the results of the ethylene-isobutylene systems and the air system.

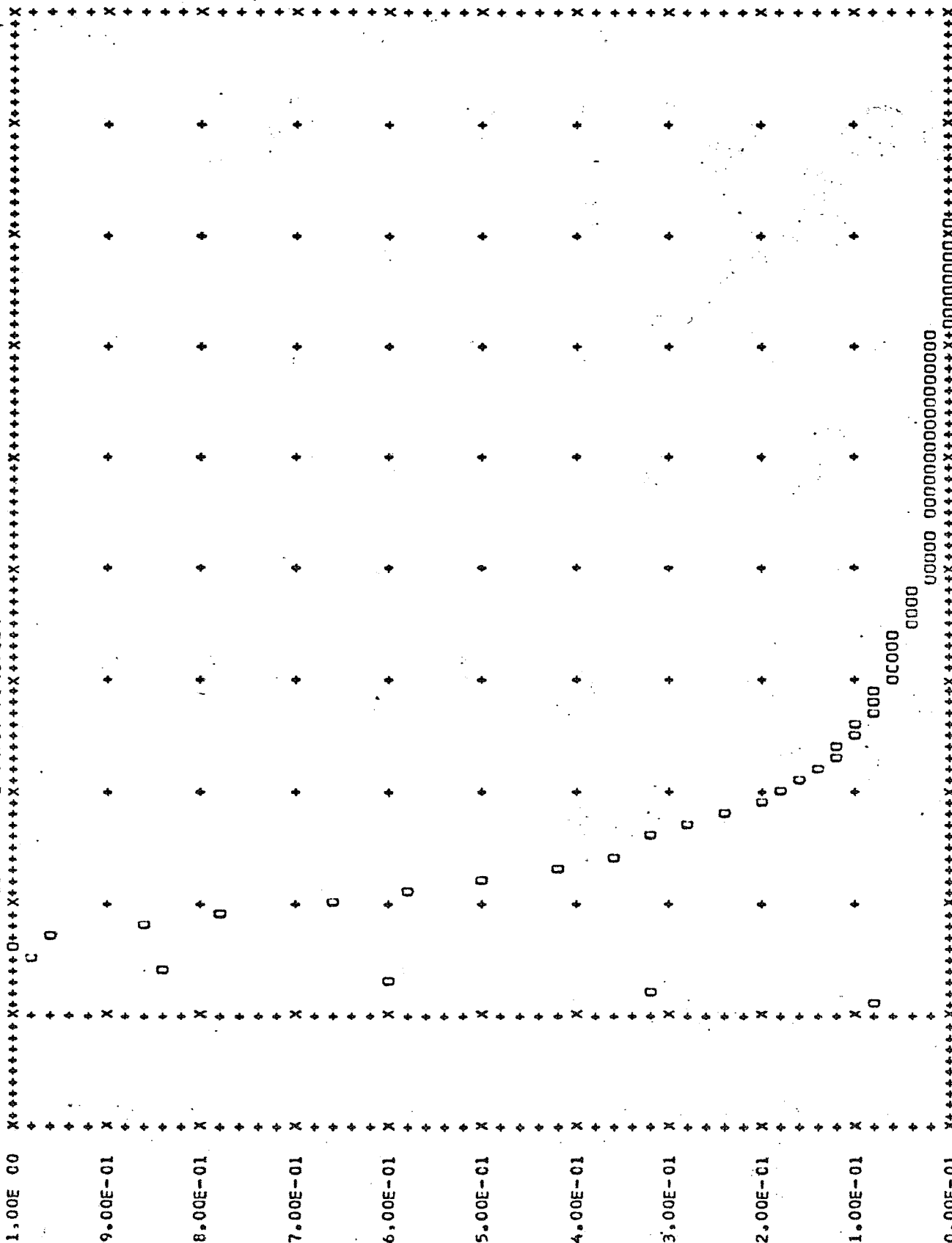
Next the temperature effects upon model prediction were studied using two system on a one meter, Chromasorb 102 column. Acetone injected by a liquid syringe and ethylene injected by the Carle valve were chosen to also confirm the previous results. The data for acetone are given in Figure 12, and those for ethylene in Figure 13. In both cases the input function is given at the beginning of the series of graphs. Because temperature effects upon gas velocity and molecular diffusivity approximately cancel, the Peclet number for both cases is approximately constant, independent of temperature.

Figure 12

Chromatograms for Acetone on Chromasorb 102

- a. Input.
- b. Chromatograms at 100°C
- c. Chromatograms at 125°C
- d. Chromatograms at 125°C (magnification)
- e. Chromatograms at 150°C
- f. Chromatograms at 150°C (magnification)
- g. Chromatograms at 175°C
- h. Chromatograms at 175°C (magnification)
- i. Chromatograms at 200°C
- j. Chromatograms at 200°C (magnification)

PLOT OF THE INPUT FUNCTION



-8.00E-01 0.00E-01 8.00E-01 1.60E 00 2.40E 00 3.20E 00 4.00E 00 4.80E 00 5.60E 00 6.40E 00 7.20E 00

THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RO= 0.223200 AND A PECLET NUMBER= 7806.000000

PLOT OF SYSTEM RESPONSE 0=IMPULSE RESPONSE, 1= CONVOLVED RESPONSE TO INPUT FUNCTION

2=ACTUAL DATA FROM GAS CHROMATOGRAPH

5.00E CO

4.50E CO

4.00E CO

3.50E CO

3.00E CO

2.50E CO

2.00E CO

1.50E CO

1.00E CO

5.00E-01

0.00E-01

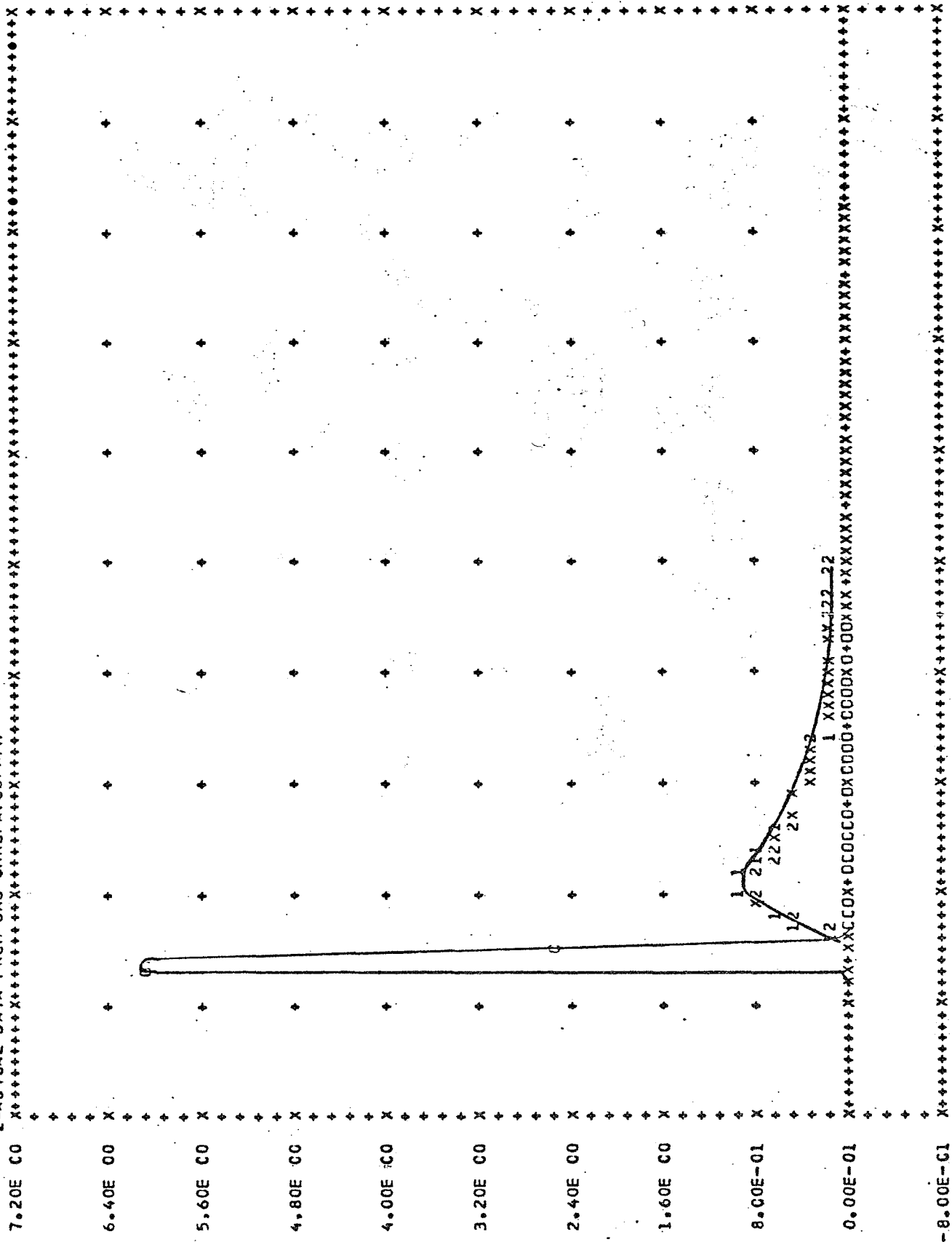
4.80E 00 5.60E 00 6.40E 00 7.20E 00 8.00E 00 8.80E 00 9.60E 00 1.04E 01 1.12E 01 1.20E 01 1.28E 01

THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RO= 0.223200 AND A PECLET NUMBER= 7806.000000

ACETONE AT 100 DEG C, 43 CC/MIN FLOW RATE, ON A CHROMASORB 102 COLUMN

PLOT OF SYSTEM RESPONSE 0=IMPULSE RESPONSE, 1= CONVOLVED RESPONSE TO INPUT FUNCTION

2=ACTUAL DATA FROM GAS CHROMATGRAPH

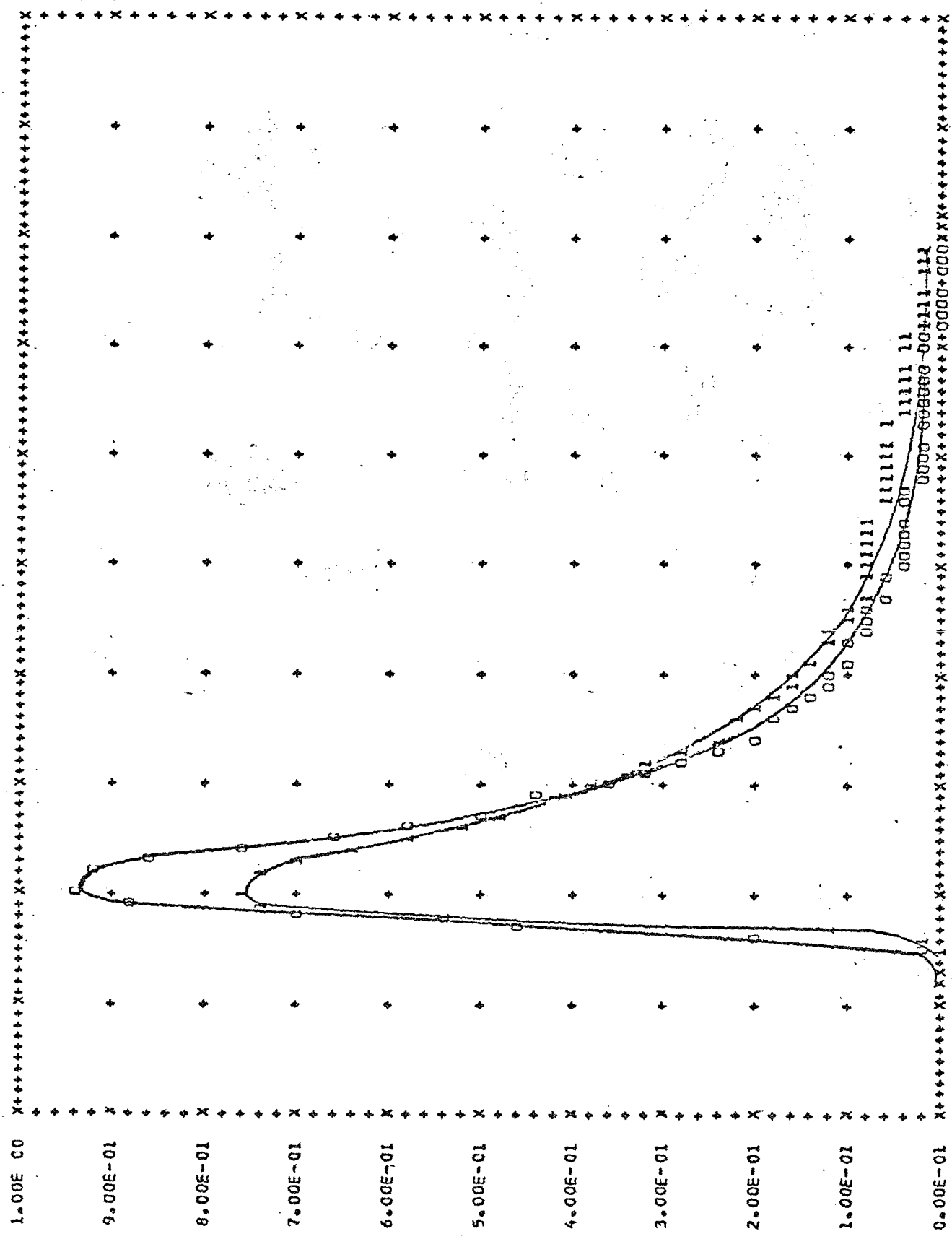


8.00E-01 1.60E 00 2.40E 00 3.20E 00 4.00E 00 4.80E 00 5.60E 00 6.40E 00 7.20E 00 8.00E 00 8.80E 00

THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RO= 1.098462 AND A PECLET NUMBER= 7806.000000

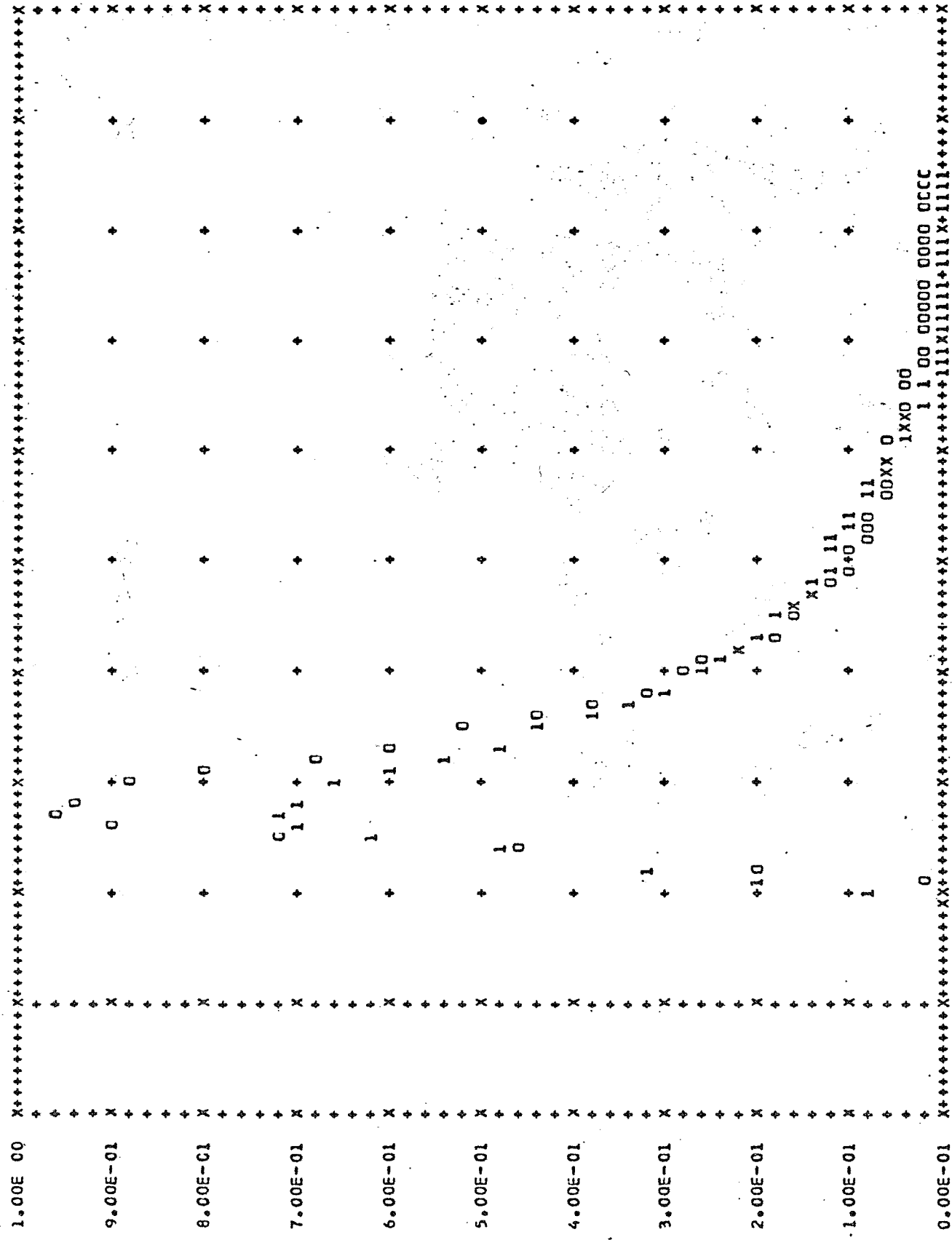
ACETONE AT 150 DEG C, 43 CC/MIN FLOW RATE, ON A CHROMASORB 102 COLUMN

PLOT OF SIMULATED AND ACTUAL SYSTEM RESPONSE, 0= SIMULATED OUTPUT, 1= ACTUAL SYSTEM DATA



8.00E-01 1.60E 00 2.40E 00 3.20E 00 4.00E 00 4.80E 00 5.60E 00 6.40E 00 7.20E 00 8.00E 00 8.80E 00
THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RD= 1.098462 AND A PECLET NUMBER= 7806.000000

PLOT OF SIMULATED AND ACTUAL SYSTEM RESPONSE, 0= SIMULATED OUTPUT, 1= ACTUAL SYSTEM DATA



[illegible]

8.00E-01 1.60E 00 2.40E 00 3.20E 00 4.00E 00 4.80E 00 5.60E 00 6.40E 00 7.20E 00 8.00E 00

THIS IS A PLCT OF Y/A VS. DIMENSIONLESS TIME FOR M RO= 4.177459 AND A PECLET NUMBER= 7806.000000

ACETONE AT 200 DEG C, 43 CC/MIN FLOW RATE, ON A CHROMASORB 102 COLUMN

Figure 13 Chromatograms for Ethylene on Chromasorb 102

- a. Input.
- b. Chromatograms at 28°C.
- c. Chromatograms at 50°C
- d. Chromatograms at 75°C
- e. Chromatograms at 100°C
- f. Chromatograms at 125°C
- g. Chromatograms at 150°C
- h. Chromatograms at 175°C

5.00E CO

4.50E CO

4.00E CO

3.50E 00

3.00E CO

2.50E 00

2.00E CO

1.50E CO.

1.00E 00

5.00E-01

10-3000

0.00E-01	8.00E-02	1.60E-01	2.40E-01	3.20E-01	4.00E-01	4.80E-01	5.60E-01	6.40E-01	7.20E-01	8.00E-01
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THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RC= 0.200907 AND A PECLET NUMBER= 7189.697CCO

0.00E-01

ETHYLENE ON A CHROMASORB 102 COLUMN, 28 DEG C, 43CC/MIN. HELIUM.

2=ACTUAL DATA FROM GAS CHROMATOGRAPH

[illegible]

7.20E CC	8.C0E CQ	8.80F CO	9.60E QO	1.04E OI	1.12E OI	1.20E OI	1.28E OI	1.36E OI	1.44E OI	1.52E OI
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THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RC= 0.132168 AND A PECLET NUMBR= 7189.699CCO

	5.00E C0	5.50E 00	6.00E 00	6.50E 00	7.00E 00	7.50E 00	8.00E 00	8.50E 00	9.00E 00	9.50E C0	1.00E 0I
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THYLENE ON A CHROMASORB 102 COLUMN, 75 DEG. C, 43 CC/MIN. HELIUM

2=ACTUAL DATA FROM GAS CHROMATOGRAPH

The graph displays the variation of the ratio of the maximum value of the function to the value of the function at the origin for different values of the parameter α . The y-axis represents this ratio, with labels ranging from $5.00E-01$ to $5.00E 00$. The x-axis represents the parameter α , with labels X at both ends. The curve starts at a high value for small α , decreases to a minimum, and then increases sharply as α approaches 1. The curve is labeled with '22222' and '111'.

4.40E C0	4.80E C0	5.20E 00	5.60E 00	6.00E 00	6.40E 00	6.80E 00	7.20E 00	7.60E C0	8.00E CC	8.40E 00
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THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RC= 0.243592 AND A PECLET NUMBER= 7189.659C00

ETHYLENE ON A CHROMASORB 102 COLUMN, 100 DEG. C, 43 CC/MIN. HELIUM

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100																																																																																																			
3.60E 00	4.00E 00	4.40E 00	4.80E 00	5.20E 00	5.60E 00	6.00E 00	6.40E 00	6.80E 00	7.20E 00	7.60E 00	8.00E 00	8.40E 00	8.80E 00	9.20E 00	9.60E 00	1.00E 01	1.04E 01	1.08E 01	1.12E 01	1.16E 01	1.20E 01	1.24E 01	1.28E 01	1.32E 01	1.36E 01	1.40E 01	1.44E 01	1.48E 01	1.52E 01	1.56E 01	1.60E 01	1.64E 01	1.68E 01	1.72E 01	1.76E 01	1.80E 01	1.84E 01	1.88E 01	1.92E 01	1.96E 01	2.00E 01	2.04E 01	2.08E 01	2.12E 01	2.16E 01	2.20E 01	2.24E 01	2.28E 01	2.32E 01	2.36E 01	2.40E 01	2.44E 01	2.48E 01	2.52E 01	2.56E 01	2.60E 01	2.64E 01	2.68E 01	2.72E 01	2.76E 01	2.80E 01	2.84E 01	2.88E 01	2.92E 01	2.96E 01	3.00E 01	3.04E 01	3.08E 01	3.12E 01	3.16E 01	3.20E 01	3.24E 01	3.28E 01	3.32E 01	3.36E 01	3.40E 01	3.44E 01	3.48E 01	3.52E 01	3.56E 01	3.60E 01	3.64E 01	3.68E 01	3.72E 01	3.76E 01	3.80E 01	3.84E 01	3.88E 01	3.92E 01	3.96E 01	4.00E 01	4.04E 01	4.08E 01	4.12E 01	4.16E 01	4.20E 01	4.24E 01	4.28E 01	4.32E 01	4.36E 01	4.40E 01	4.44E 01	4.48E 01	4.52E 01	4.56E 01	4.60E 01	4.64E 01	4.68E 01	4.72E 01	4.76E 01	4.80E 01	4.84E 01	4.88E 01	4.92E 01	4.96E 01	5.00E 01	5.04E 01	5.08E 01	5.12E 01	5.16E 01	5.20E 01	5.24E 01	5.28E 01	5.32E 01	5.36E 01	5.40E 01	5.44E 01	5.48E 01	5.52E 01	5.56E 01	5.60E 01	5.64E 01	5.68E 01	5.72E 01	5.76E 01	5.80E 01	5.84E 01	5.88E 01	5.92E 01	5.96E 01	6.00E 01	6.04E 01	6.08E 01	6.12E 01	6.16E 01	6.20E 01	6.24E 01	6.28E 01	6.32E 01	6.36E 01	6.40E 01	6.44E 01	6.48E 01	6.52E 01	6.56E 01	6.60E 01	6.64E 01	6.68E 01	6.72E 01	6.76E 01	6.80E 01	6.84E 01	6.88E 01	6.92E 01	6.96E 01	7.00E 01	7.04E 01	7.08E 01	7.12E 01	7.16E 01	7.20E 01	7.24E 01	7.28E 01	7.32E 01	7.36E 01	7.40E 01	7.44E 01	7.48E 01	7.52E 01	7.56E 01	7.60E 01	7.64E 01	7.68E 01	7.72E 01	7.76E 01	7.80E 01	7.84E 01	7.88E 01	7.92E 01	7.96E 01	8.00E 01	8.04E 01	8.08E 01	8.12E 01	8.16E 01	8.20E 01	8.24E 01	8.28E 01	8.32E 01	8.36E 01	8.40E 01	8.44E 01	8.48E 01	8.52E 01	8.56E 01	8.60E 01	8.64E 01	8.68E 01	8.72E 01	8.76E 01

ETHYLENE ON A CHROMASORB 102 COLUMN, 150 DEG. C, 43 CC/MIN. HELIUM

0.00E-01

THIS IS A PLOT OF Y/A VS. DIMENSIONLESS TIME FOR M RC= 0.271200 AND A PFCLET NUMBER= 7189.699000

ETHYLENE ON A CHROMASORB 102 COLUMN, 175 DEG. C, 43 CC/MIN. HELIUM

Consider the acetone data first, as shown in Figure 12. In general, the ability of the model to depict the data accurately increases as the temperature is increased. As expected from heat of adsorption concepts discussed earlier, the retention or peak times decrease as the temperature increases. In this system, the thermodynamic parameter mR_0 increases from 0.223 at 100°C to 4.18 at 200°C as expected. At temperatures of 125°C and higher, the representation of the data by the model appears quite acceptable for design purposes.

The ethylene data shown in Figure 13 show the same effect, although it is more pronounced. In fact, at the highest temperature studied, 175°C the predicted chromatogram deviates appreciably from the actual data.

Both the acetone and ethylene data were obtained on the same type of column, a Chromasorb 102 porous polymer, under similar conditions. Because the Peclet numbers will be similar in both systems, it appears that an unknown transport mechanism which is temperature sensitive as well as material dependent is responsible for the differences between the data and the prediction. Because the solid is a porous polymer, it is possible that the original assumption of a thin adsorbed layer on the adsorbent surface and no intraparticle diffusion is not valid. This might account for the differences between the observed differences between the acetone and ethylene systems because ethylene is a smaller molecule and would tend to exhibit larger intraparticle diffusion effects. The use of the more complicated model which includes the transport parameter N_{tOG} offers a possible area of study. The term N_{tOG} itself is relatively temperature-insensitive but interactions

between the various system parameters Pe , mR_0 and N_{tOG} may be sufficient to account for this behavior. These topics will be investigated thoroughly in future work.

The technique of numerically convoluting the theoretical impulse response with the input pulse as measured experimentally appears to be satisfactory. The results are qualitatively correct, and the areas computed under the convolved response using normalized data, deviate from unity by less than 0.1%. Finally, the program through adjustment of mR_0 is able to match the times of peak appearance for the model and data in an efficient manner. This allows for the comparison of the models solely on their ability to accurately describe the sample dispersion which appears now as a most important factor in reliable system prediction.

VII. CONCLUSIONS

The data reduction program, in its present form is capable of generating simulation of a gas chromatograph then comparing that simulation to actual system data. The program is capable of convoluting any model derived thus far, and allows for the addition of added variables such as N_{tOG} to give a better simulation.

There are still integration problems in the program if the number of points to be integrated is small and the curve is peaked. This is a problem inherent in finite point integration, and is solved by considering more points. However, the program is limited to 1500 time increments because of restrictions in the WATFOR compiler used. FORTRAN G and H compilers are available, but the RPPILOT subroutine will not function with these units.

The equilibrium adsorption model, a simple, two parameter equation was evaluated with data to check the data reduction program. It was found that the model exhibited the basic characteristics of the data, but under certain conditions it did not predict the disperse data. It was found that prediction was more satisfactory at higher temperatures, suggesting a temperature-dependent transport mechanism which is sensitive to the samples considered. A likely candidate is the intraparticle diffusion of the sample. Future model work will proceed in this direction using the data reduction program to compare theory with experiment.

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IX. APPENDIX A - Data Reduction Program

1. Variable Listing
2. Data Input Instructions
3. Program Flow Diagram
4. Program Listing

The appendix was not included in the report because of its length. A copy may be obtained upon request from:

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